ATOMIC FORM

with

Special reference to the Configuration

of the

CARBON ATOM

BY

EDWARD E. PRICE

THE CARBONOID

SPIRAL CHAIN
Shewing right and left handed Configurations.

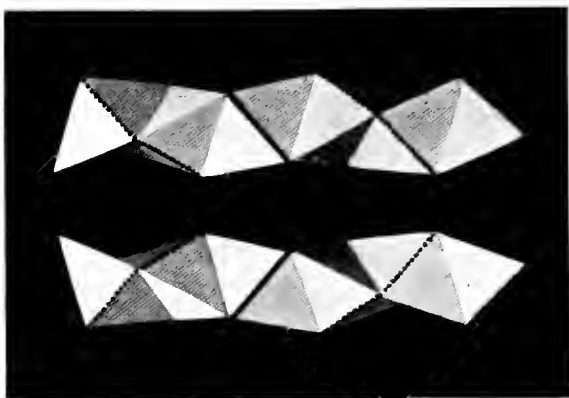"Are the atoms of Tartaric Acid arranged along a spiral of a right-handed screw, or are they situated at the corners of an *irregular* Tetrahedron, or have they some other asymmetric grouping ? Time must answer this question. But of this there is no doubt, that the atoms possess an asymmetric arrangement like that of an object and its mirrored image. Equally certain is it that the atoms of the left-handed Acid possess just the opposite asymmetric arrangement."

PASTEUR.
LEÇONS DE CHIMIE, 1860.

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PREFACE

I T is more than 20 years ago that the author was first
led to the consideration of the Theory of Atomic
Form, and shortly afterwards commenced to make
models of tetrahedra of various forms with the view of
ascertaining how far such a figure would be capable
of fulfilling the rôle of the carbon atom. The author
concentrated his attention upon the form of an irregular
tetrahedron, particulars of which are given in the pages
of this book, and large numbers of models of this form
have been made, and combined in various ways in order
to represent the various types of carbon compounds.

The work was suspended in 1914 by the exigencies
of the War, and the urgent demands of a professional
business; hence the delay in submitting the results to
public estimation.

At the present time the constitution of the Atom is
the subject of physical theories which are widely separa-
ted from the ideas which have been set out in this book,
and many persons may be disposed to lay it aside as
being inconsistent with the latest advances of scientific
thought. The author asks for a more impartial con-
sideration of this subject; so much has yet to be dis-
covered, so many problems have yet to be elucidated,
that no Theory should be rejected which helps in any
way the consideration of these problems.

It is also suggested that some persons who may not at present see their way to accept the theory of Atomic Form, may yet find the models of aggregates of the carbonoid an assistance when considering some of the problems of Organic Chemistry—by enabling them more easily to visualize the structures in three dimensions which undoubtedly are represented by chemical formulæ.

The author desires to thank Mr. I. D. Margary, M.A., who has read the manuscript, for his kind assistance and many valuable suggestions.

THE HAVEN,
    DORMAN'S PARK,   EDWD. E. PRICE.
        SURREY.

July, 1922.

CONTENTS

CHAPTER I.

INTRODUCTORY

IN any discussion of the constitution of the Atom the phenomenon of crystallization must have an important place, and it may be justly said that no theories of atomic or molecular constitution, which ignore the facts connected with the crystallization of the Elements, can be considered as resting on a sound basis.

When an elementary substance is in a gaseous condition enclosed in a vacuum tube and subjected to forces relatively of great magnitude, there must necessarily be great difficulty in separating the phenomena produced by these conditions and by the rapid movements (both rotational and translatory) of the atom, from those characteristics that belong exclusively to the atom itself. If these characteristics are studied when the atoms are in a state of approximate rest, they afford a much more satisfactory field for investigation, and more reliable results may be expected.

The following statement of facts in connection with the crystallization of elementary substances is submitted.

(1). A large proportion of the Elements are known to assume a crystalline structure when in the solid state, and of those which are not so known, many are capable of forming crystalline space-lattices when in combination with other Elements.

Some elementary substances which are liquid or gaseous at Ordinary Temperatures, may not have been examined in the solid state under conditions which produce the crystalline form.

(2). Of those Elements which are known to crystallize each one forms its own particular crystal or space-lattice. Some elements crystallize in more than one geometric form, but these cases do not invalidate the general rule stated above.[1]

(3). Crystal formation is not affected or controlled in any way by physical forces other than heat, pressure and solubility. Electricity plays no part in the formation of a crystal, and a magnetic field has no effect upon the process.

(4). The space-lattices vary as regards density ; *i.e.*, the atoms are more closely packed in some crystals than in others. Sulphur forms crystals in two forms—Rhombic and Monoclinic, the latter readily changing into the Rhombic form with a marked change of volume at the transition point.

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[1] Von Weimarn " *Kolloid Zeitschrift* " Vol. II. p. 81, (1907), has put forward the view that even gases have a micro-crystalline structure in their particles. According to him all matter is crystalline, and what we call amorphous materials are only so to us, because we cannot see the extremely tiny crystals from which they are irregularly built up.

It is difficult to conceive of spherical or ellipsoidal forms having the power to arrange themselves according to geometric laws so soon as the vibrations of heat are reduced to a certain degree, and in the absence of any other directive force so far as is at present known, but if the atoms themselves have definite geometric forms, then arrangement in an orderly space-lattice, so as to produce definite geometric figures peculiar to each atom, appears to be the natural result of the withdrawal or reduction of the vibrations of heat.

It should be borne in mind that in Nature the permanent spheroidal form is either the product of living agencies or of rotational movements, and is never associated with matter in its elementary state.

The heavenly bodies owe their shape to their rotation around their axes. The fruits and seeds of the Earth are the products of vegetation, and the rounded forms of organic life on sea and land are again the result of living energy. The rounded forms of the pebbles on the sea shore are the result of the ceaseless movement of the waves. Drops of water and other liquids owe their shape to the movement of the drop in passing through the air, and cannot permanently retain the spheroidal form.

Geologists are familiar with rounded and spherical forms, but these when carefully considered will generally be found to arise either from organized living forms of past ages, or to meteorites which have fallen upon the earth's surface, and which attained their

spherical shape when in a molten condition by rapid transit, and probably by a rotational movement.

Atoms when in a gaseous state, and rotating rapidly, will occupy a sphere of influence which will assume a spheroidal or ellipsoidal form, but the atoms themselves, when at rest, must be considered in the light of the crystals which they then form, and must have such forms as will enable them readily to build up the space-lattices of their own particular crystals. The crystals thus formed will not necessarily coincide in form with the atoms of which they are built up, but may differ entirely from the form of the atoms of which they are composed.

Consider also the great diversity in the characters and qualities of the various Elements. Large differences in melting and boiling points and in other chemical and physical qualities characterize Atoms of Elementary Substances, whose atomic weights are in near proximity, as, for instance, Carbon with atomic weight 12 and Nitrogen with atomic weight 14.

It is generally conceded that we must assume one general substance as the basic material out of which all atoms are constructed, and if that be so, it is impossible to attribute these diversities to difference in essential character of the material of which they are made up. Taken alone the atomic weights are insufficient to explain these diversities, and we are consequently led to look to differences of *form* as the most natural explanation of this great diversity of character.

It would also be difficult to conceive of this large number of distinct atoms each with its own atomic weight, valency, and its group of qualities and affinities, but without form.

The Theory of Atomic Form does not exclude the possibility of each atom being constructed of a large number of very small particles or corpuscles, or, as we prefer to designate them, " sub-atoms," which may constitute the " materia prima " out of which all atomic bodies are constituted. Such a view would be quite consistent with the arrangement of these sub-atoms so as to form a number of geometric forms, but if such be the case, it seems probable that the sub-atoms are in close contact without any interspaces such as we find in the space-lattices of crystals. A truly solid figure of this class would necessarily have great stability, but might be broken up in a vacuum-tube when under the influence of strong electric or other forces.

There appears to be great difficulty in reconciling the Electronic Theory of the constitution of the Elements with the considerations stated above. The suggestion that the atom is a system of negatively-charged corpuscles revolving around a positively-charged centre cannot readily be reconciled with the power which each Element possesses of building up its own crystalline form with its great stability, sharp edges and smooth faces. Such a conception of atomic structure appears to be at variance with our knowledge of crystal structure, and fails to assist us with the many problems of organic chemistry by which we are still confronted.

According to a recent publication by Stewart, the Electronic Theory has not been generally adopted by organic chemists ; he writes :[1]

"It seemed as though the discoveries in Electronic Physics would have their reaction upon our structural views ; but though several attempts have been made in this region of the subject, Organic Chemists in general have not welcomed them with anything like whole-hearted encouragement. There is a feeling apparently that in abandoning the usual structural formulæ and replacing them by electronic symbols, the subject is being complicated instead of simplified ; and this feeling, whether it be due to scientific caution or to mere conservatism, has certainly carried the day for the present."

It is suggested that until the electronic constitution of matter is brought more into accord with the phenomena of Organic Chemistry, we are at liberty to consider any other theory that seems likely to assist in the solution of the problem.

The task of assigning definite geometric form to each Element and agreeing such form with the known atomic weights, valencies and other characters of the element, is surrounded with many difficulties. At present we propose to consider only the element Carbon, which, by reason of the extraordinary number and variety of its compounds, reveals its character more than any other atom, but in the first place we offer a few words on the possibility of designing a geometric form suitable for mono-valent and di-valent Elements.

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[1] Stewart—" *Recent Advances in Organic Chemistry*," (1920), page 2.

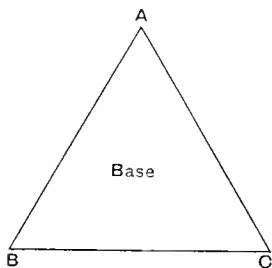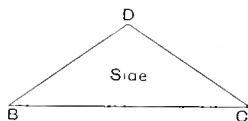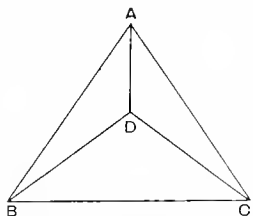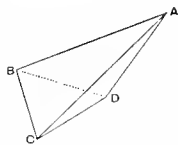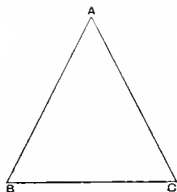## Suggested possible form of a MONOVALENT ATOM

Fig. 1   Base.

Fig. 2
One of the 3 sides
surrounding the apex

Fig. 3
Stable position attached
by base

Fig. 4
Unstable position, attached by
one of the 3 sides meeting
at the apex D

Suggested possible form of a DI-VALENT ATOM
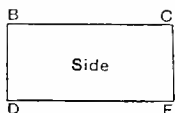

Fig. 5
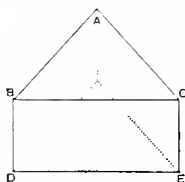Base of Prism

Fig. 6

Sides of Prism

Fig. 7

Form of Prism with triangular
Base as above.
If the base be enlarged the sides
will be longer and narrower.

A possible model of a Hydrogen Atom can be pre-
pared, see Figs. 1 to 4. The form is a very oblate
pyramid with a base smaller than the face of
the carbon atom. It can form stable attachment
with Carbon or Oxygen, etc., *only by the base*, but that
is large enough to prevent the attachment of any other
Element. Two such figures, united by the base, form
a small but compact figure which might represent a
molecule of Hydrogen Gas, and in that condition it
will not readily unite with any other Element.

A model of a di-valent Atom can also be prepared.
See Figs. 5 to 7.

When submitting these figures it is to be clearly
understood that they are merely guess-work efforts,
much more study and research being necessary before
the true forms can be established, but they are intend-
ed to shew that models of mono- and di-valent atoms
are not impossible.

It will be asked, how can the suggested hypothesis
of Atomic Form be reconciled with the present theories
of Valency ?

It is suggested that Valency consists of the ability of an Element to attach itself to other atoms either of the same or some other Element and is dependent upon the number of faces of its geometric figure, which are available for making stable attachments. No solid figure can have less than four faces, but it may be of such a form that only one, or it may be, two of its faces are so situated or of such a size and shape as to be capable of forming a stable attachment.

Moreover, in each particular case, the possibility of such an attachment must depend upon other conditions, namely, the form of the atom to be attached and the relative movements of the two atoms and their axis of rotation, if in the gaseous condition.

A great amount of study and research will be necessary in order to design forms which shall comply with the known requirements of the doctrine of Valency, but it is contended that such forms can be designed and the requirements met.

The so-called " *double bond* " between adjoining Carbon Atoms deserves special notice. There appears to be no definite evidence that the Carbon Atoms are really united by a double or treble linkage. On the contrary, the carbon chain breaks more readily at this point than elsewhere, and the carbon compounds containing a so called "*double bond* " readily take on additional atoms or groups. The term "*double bond*" is, in reality, a "*figure of speech* " which expresses the fact that two unsaturated valencies exist in regard to two adjoining carbon atoms.

It is submitted that the form of the carbon chain and its rotational movement fully account for the occurrence of such unoccupied faces in *pairs*, and generally on adjacent carbonoids. The matter will be more fully dealt with in Chapter V., under the heading of " Law of even numbers," and in Fig. 26, page 38a, where the pairs of faces are shewn.

These observations refer to carbon compounds where the unsaturated valencies of adjoining Carbons are held to satisfy one another, such as Ethylene and Acetylene, but there are other cases where " *double bonds* " are held to exist between Oxygen and Carbon, as in the Aldehydes and Acids.

These cases are peculiar by reason of the fact that so long as di-valent oxygen is in the form of a hydroxyl group, and has only one free valency, it functions towards Carbon as a mono-valent atom, but if the hydrogen be removed from the Hydroxyl, the oxygen is supposed to act as a *di*-valent atom, and appears to be capable of satisfying two carbon valencies.

It is suggested that the conduct of Carbon, Oxygen and Hydrogen in these positions can only be properly understood when the geometric forms of all the three atoms are known, and their interactions clearly portrayed.

The hypothesis of Atomic Form adopts the following conceptions with regard to elementary Atoms, viz. :

(1). The Atom has a definite geometric form which distinguishes each Element from all others.

(2). Atoms belonging to the same group in the Periodic Law differ in magnitude but may have the same or similar forms.

(3). The valency of an Element is the number of faces available for stable attachment to other atoms of the same Element or to atoms of some other Element.

(4). The geometric form of the atom confers upon it its characteristic qualities and powers.

(5). Except at $0°$ on the absolute scale of temperature all atoms must be considered to be in motion, either vibratory or translatory. In the case of gases the molecules are considered to have both rotational and translatory movement.

The adoption of the above conceptions is no doubt difficult, in view of the regularity of the differences of valency and Atomic weight of the groups in the Periodic Table of the Elements, and the similarity of the several increases in atomic weight. This matter will be further considered in Chapter XII, "Concluding Observations."

The remaining chapters of this book will be devoted to the consideration of the possible form of the element Carbon, and an attempt will be made by models of the Carbon framework of various compounds, to shew the agreement between these models and the known facts with regard to the compounds which they represent.

CHAPTER II.

THE CARBONOID AND ETHYLOID

To attempt the design of a geometrical solid which may fitly represent the Carbon Atom, is a task of considerable difficulty.

The universal tetravalent character of carbon compels us to suggest a tetrahedron for the model, but there are a large number of tetrahedra, any one of which might be adopted. In view, however, of the equality of the four valencies we are led to adopt a figure in which all the faces are equal, but we have still a large number of forms available, dependent upon the character of the face adopted. The formation and stability of the Benzene Nucleus suggests that the tetrahedron should be of such a form that six atoms can combine to produce a new figure. Only one figure can now be designed which will fulfil all our requirements.

Accordingly, we submit the model, Fig. 8, which will be called a carbonoid. Its features are :

(1). All the faces are alike in every respect, and stand in the same relationship to one another.

(2). There are two equal solid angles, A C and B D in Fig. 8, and four other solid angles equal to one another, but differing from the other two ; the two equal solid angles are each 1/6th part of four right-angles, so that the angle at E, Fig. 8, is an angle of 60°.

(3). The faces are isosceles triangles, and they have the peculiarity that the base is equal to the normal to the base. See Fig. 9.

(4) If the figure be divided into two equal portions by a plane passing through one of the triangular faces, B—D, and also through a point bisecting the opposite solid angle at E, such plane will be an equilateral triangle. See Fig. 8.
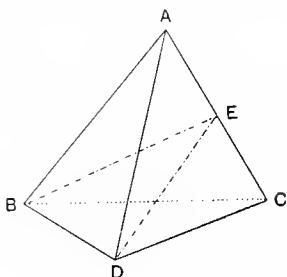

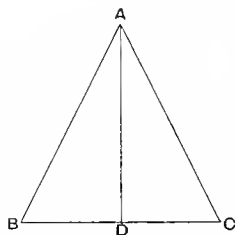Fig. 8   The Carbonoid
B.D.E. is an equilateral Triangle

Fig. 9
Face of Carbonoid
A.D.=B.C.

It will be admitted that this figure, the " Carbonoid" has some special features— more than the regular Tetrahedron— and it seems impossible to design any other figure which will be so simple and at the same time so symmetrical.

If two carbonoids are joined together by *any* of their faces, a new six-sided figure is produced, which is called an " *Ethyloid*." See Fig. 10, p. 14. It differs materially from the carbonoid and from any other combination of carbonoids. There is nothing at all like it among the models which contain three or more

carbonoids. There is now a slight difference in the position of the faces, which are arranged in pairs. Two pairs are alike in their positions relatively to one another,
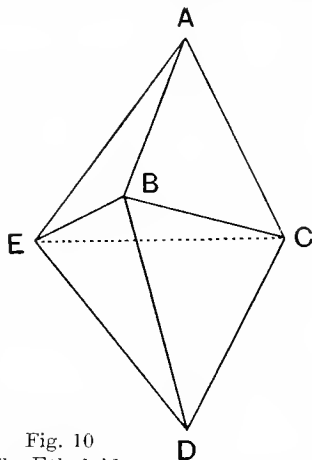

Fig. 10
The Ethyloid

and to the rest of the figure, viz., A E C, D E C and A B C, D B C, but the third pair, A B E and D B E, are differently placed, the solid angle at B E dividing the two faces, being situated nearer to the centre of the figure, the line B—E forming the bases of the two isosceles triangles. This is called a *co-basal* pair of faces.
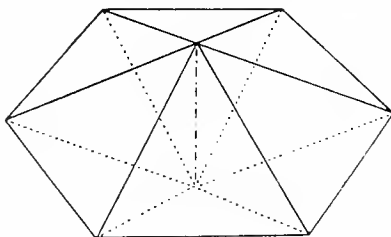

Fig. 11
The
Benzenoid

If six carbonoids or three ethyloids are joined together in regular order, a new figure is obtained, called a " *Benzenoid*," Fig. 11, which has twelve faces, all exactly alike, and all occupying similar positions in the figure. This is a very compact and symmetrical figure, and should have great stability and special features and characteristics separating it from all other combinations of either Carbonoids or Ethyloids.

We will consider presently the models of Carbon Chains, in connection with which there are some interesting features, but first let us consider the model of the " *Ethyloid*."

Every Chemist will allow that the Ethylene group occupies a very important position in Organic Chemistry. It is the basis of a large number of substances both useful, important and abundant. In an homologous series it is the compound containing two Carbons only that usually occupies the most important place in the series. Moreover, the *Ethyl* group occupies an important position in a large number of substances and we notice its stability in the Ethers.

The importance of this group is shewn by the following Table of Compounds of two Carbons :—

Ethane	$C_2 H_6$	
Ethylene	$C_2 H_4$	The principal constituent of Coal Gas.
Acetylene	$C_2 H_2$	
Ethyl Alcohol	$C_2 H_5$ OH	The Alcohol of Commerce.
Acetaldehyde	$C_2 H_4$ O	

Acetic Acid	$C_2 H_4 O_2$	The commonest monobasic acid.
Oxalic Acid	$C_2 H_2 O_4$	The commonest di-basic acid.
Di-ethyl Ether	$C_2 H_5 O C_2 H_5$	The commonest Ether
Cyanogen	$C_2 N_2$	

The Ethyloid is more convenient in shape than the Carbonoid and far exceeds in symmetry and compactness all the other groups. It should have great stability. It is significant that this form coincides with a group so widely known and of such general usefulness, and occupying such an important position in Organic Chemistry.

The position of the acids of two Carbons only is further shewn by considering the Diagrams of melting points of the monobasic and di-basic acids, which are given in Holleman's "Organic Chemistry", Fifth Edition, pages 106 and 199. In these two Diagrams the lowest melting point coincides with a chain of 5 carbons, there being a remarkable fall between the acid containing 4 and that containing 5 carbon atoms. Throughout the two series there is a fall as we pass from even to odd numbers, and a marked recovery on returning from odd to even. Another remarkable feature is the high melting-point of the acid containing two carbons only. Some of the figures are now given :

		Monobasic Acid	Di-basic Acid
One carbon		+ 8·3	
Two carbons	up	+ 16·7°	+ 189·5

			Monobasic Acid	Di-basic Acid
Three carbons	down	— 22 °	+ 133·0
Four ,,	up	— 3·1	+ 183·0
Five ,,	down	— 58·5	+ 97·5
Six ,,	up	— 1·5	+ 153·0
Seven ,,	down	— 10·5	+ 105·5
Eight ,,	up	+ 16·5	+ 140·0

In the case of the Paraffin Series where there is no acid radicle attached, the lowest member of the series contains only three carbons. See Diagram Fig. 12, p. 18. The anomalous position of the compound containing two carbons is, however, continued in this Diagram, thus confirming the unique position occupied by all compounds of two carbons only, which is associated with the form of the Ethyloid.

It is noticeable also that the special form of the Ethyloid is associated with a high melting point, because there is reason to believe that compounds of symmetrical and compact form are distinguished by higher melting points.

In Stewart's *Stereochemistry*,[1] the following statements are made:

" In 1882 Carnelly stated that of two isomers, that which possessed the most symmetrical and compact structure was distinguished by having the higher melting-point and Franchimont has brought evidence in favour of this view. . . . Werner puts forward the idea that this difference in melting-point may be merely one instance of a much more general rule." . . . .

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[1] Stewart—" *Stereochemistry*," (1907) pp. 174/5.
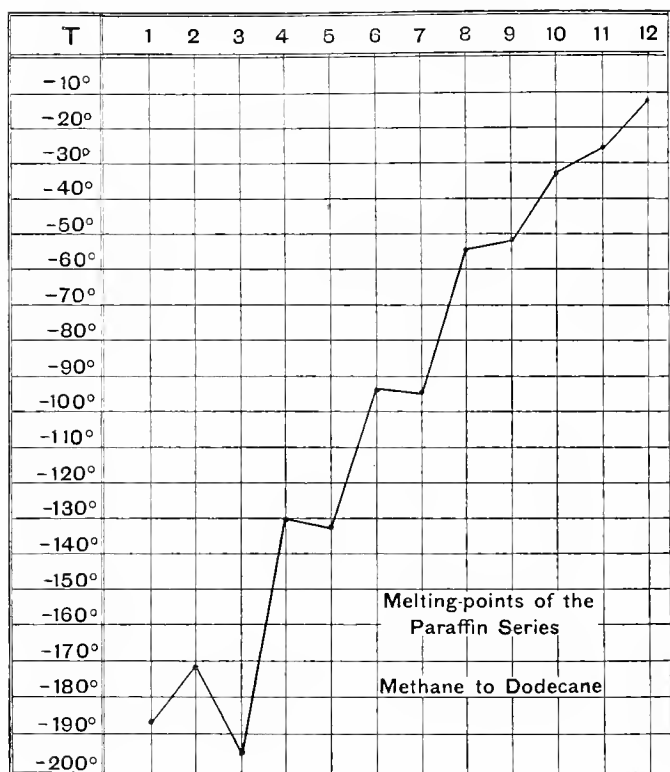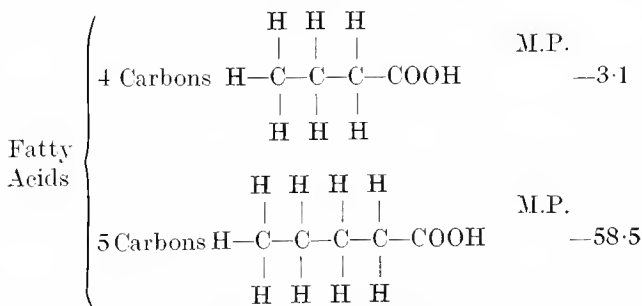
NUMBER OF CARBON ATOMS.

Fig. 12

In this Chart, the compound containing 3 carbons has the lowest melting point. In the Fatty and Di-basic Acids, there is a heavy fall between 4 and 5 Carbons, and the compound containing 5 carbons is by far the lowest of the series.

" This idea may prove to be based upon mere coincidence, but the fact that benzene para-derivatives have higher melting-points than the corresponding ortho-derivatives seems to point to some general rule such as Werner foreshadows."

In the Second Edition, under " *The properties of Ethylene Stereoisomers.*"[1]

"Carnelly's rule that the higher melting-point is generally associated with symmetry and compactness of structure finds an illustration in the fact that axially-symmetrical ethylene isomers have melting-points higher than those of the plane-symmetrical type. They are also less soluble and less volatile; and they appear to have higher densities."

The Theory of Atomic Form receives some confirmation from the differences of melting points between those acids containing an even and those of an uneven number of carbon atoms. If the carbon atom be supposed to be a sphere or cube it is difficult to understand why such large differences should exist, thus :—

Fatty Acids
$$
\begin{array}{l}
\quad\quad\quad \text{H H H} \\
\quad\quad\quad |\ \ |\ \ | \quad\quad\quad\quad \text{M.P.} \\
\text{4 Carbons } \text{H—C—C—C—COOH} \quad\quad -3{\cdot}1 \\
\quad\quad\quad |\ \ |\ \ | \\
\quad\quad\quad \text{H H H} \\
\\
\quad\quad\quad \text{H H H H} \\
\quad\quad\quad |\ \ |\ \ |\ \ | \quad\quad\quad \text{M.P.} \\
\text{5 Carbons } \text{H—C—C—C—C—COOH} \quad -58{\cdot}5 \\
\quad\quad\quad |\ \ |\ \ |\ \ | \\
\quad\quad\quad \text{H H H H}
\end{array}
$$

[1] Stewart—"*Stereochemistry*," 2nd Edition, (1919), p. 118.

If four Carbons are represented by four spheres and an additional sphere is introduced into the Carbon Framework of the Acid, producing a *fall* in the melting point of 55°, it is inconsistent that the introduction of a further sphere should produce a *rise* in the melting point of 57° to −1·5°.

When, however, the chain of carbonoids is inspected, see Fig. 26, p. 38a, we see that the introduction of an additional carbonoid produces considerable change in the position of the end carbonoid to which the acid radicle is attached, the effect of this alteration being to reverse the position relatively to the rest of the chain of the end carbonoid, and the attached acid radicle. This change may well be sufficient to alter materially the relationship between the carbon chain and the acid radicle, and thus give rise to a change in the properties of the substance.

It will be seen that the differences of melting points are much larger in the case of the Acids than they are in the diagram of the Paraffin Series, shewing plainly the effect of the Acid Radicle, but these differences persist in the case of the Paraffin Group, indicating that the cause of the differences in character is to be found in the Carbon Chain, and that the function of the Acid Radicle is to enhance the effect of this peculiarity. An important feature of the Carbonoid Chain is the change in the position of the end Carbonoid taking place at each change in the number of carbons in the chain, with a more or less marked reversion to the old positions when we get back to the corresponding odd or even number of carbons.

This may furnish us with an explanation of the variations in melting points of these compounds.

# CHAPTER III.

BENZENE AND SOME OF ITS DERIVATIVES

The Benzenoid, Fig. 11, p. 14 is a completely symmetrical figure and admits of no division into right-handed and left-handed isomers—optical activity, such as arises when asymmetry exists, is therefore impossible.

Among Benzene derivatives it is generally the case that all those which do not involve the existence of an attached chain of two or more carbonoids (added to the Benzenoid at the same point) are inactive, and the Benzene Ring, with the addition of a single atom, other than Carbon, will also be inactive, thus :
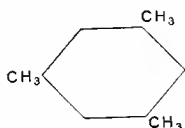
I. INACTIVE   II. POSSIBLY ACTIVE
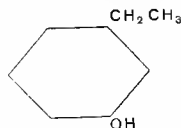
CH_3 in No. I. is attached to the Ring so as to lie not in the plane of the paper but at right angles thereto, and in No. II. CH_2 occupies a similar position. CH_3 in No. 2 is again approximately in the plane of the paper, and may be on the right hand or the left.   See Fig. 13, p. 22, A and B representing the enantiomorphous forms of the two isomers.
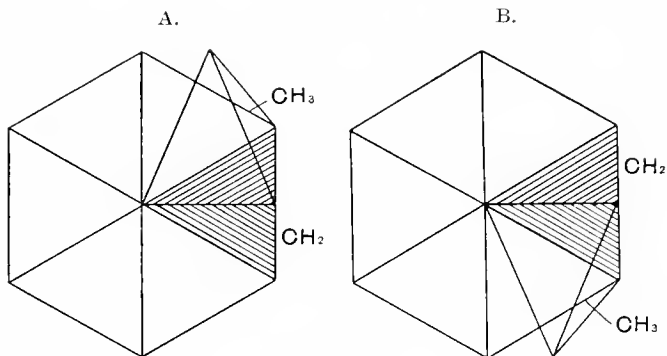
Fig. 13

The two isomers of No. II. cannot be made to corres-
pond.   In one of the isomers the $C H_3$ group will be
on the side nearer to the O H group, and in the other
it will be on the other side and further from the hydroxyl.

This Form is described as "*possibly*" active, because
if the carbonoids forming the chain are differently
arranged, no right and left-handed isomers will exist,
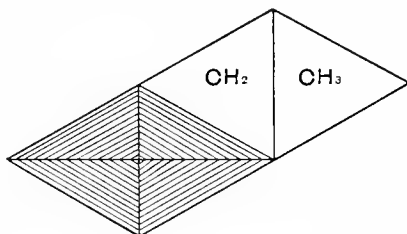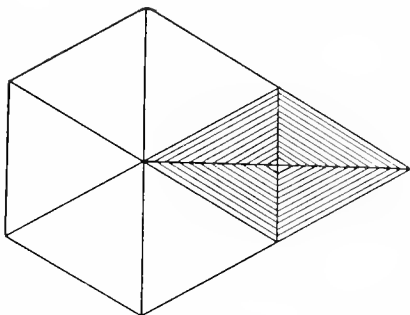the arrangement being symmetrical, thus :

Fig. 14
Perpendicular View

Fig. 15
Horizontal View

These facts concerning the inactivity of Benzene and its derivatives are borne out by experimental data. In Cohen's " *Organic Chemistry*," it is stated that there is no asymmetry in Benzene and no optical enantio-morphs[1] :

"All attempts to resolve Benzene Compounds have been fruitless, and what is even more significant ; there is no single instance of an optically active compound of Benzene, among the many derivatives found in Nature, which owes its activity to the asymmetry of the nucleus."

It is not only necessary to produce a model of six Carbonoids which will correspond with the known characters of Benzene, such as the entire absence of enantiomorphism, but our model should explain the unsaturated condition of the molecule, and the fact that only six out of the twelve faces are occupied by Hydrogen.

[1] Cohen—*Organic Chemistry*, 1st Edition, p. 446.

It is assumed that the figures of Carbon and its compounds when in the gaseous state are floating in a medium which supports them in much the same way as water supports any objects floating in it, and that the molecules are subject to the same laws of gravity and mutual attractions as are observable in other and larger objects.   If it be allowed that the Hydrogen Atom has the form of a very oblate pyramid, it will follow that nascent Hydrogen will adopt a position in which the base of the pyramid will be above and the apex will occupy the lower position thus :
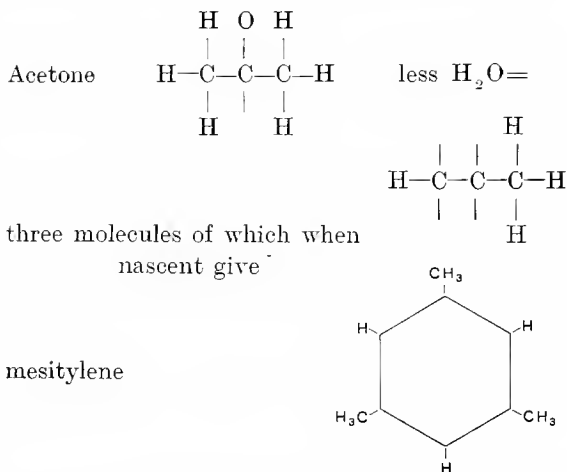
Base

Apex
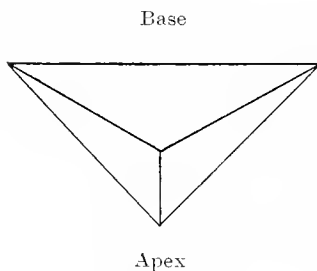
Fig. 16

In this position the Hydrogen Atoms will readily combine with the lower surface of the Benzenoid, but it will be practically impossible for them to make stable attachments to the upper surface ; to do so it would be necessary for the Hydrogen to make a complete inversion of its position so that the base may be below and the apex above, such a change of position would be unlikely.   In this view, it would be the *upper* surface of the Benzenoid which would be free from Hydrogen.

It may be argued that if the Hydrogen Atom was so placed as to be unable to attach itself to more than one side of the Benzenoid, would not this fact also prevent the union of two Hydrogen Atoms to produce a molecule of Hydrogen Gas, but it will readily be seen that in such a combination we have two atoms of Hydrogen concerned, both of which would be disposed to move towards each other and only one half of the inversion of each atom would be necessary to enable a stable union between the two atoms to take place by attachment of their bases.

When the Benzene Nucleus is formed by the coming together of three Ethyloids, freed from Hydrogen, an atmosphere of nascent Hydrogen will surround the Benzenoid, and the under surface thereof may be supposed to obtain immediate attachment of Hydrogen ; but the upper surface may remain free to form attachment to other atoms if such are in a nascent condition and occupy suitable positions. The subsequent conduct of the Benzene Nucleus may depend upon the character of the atom with which it is brought into contact, and the circumstances such as heat, pressure, etc., existing at the time, together with the peculiar movements rotational and otherwise of both groups relatively to one another.

BENZENE DERIVATIVES

Certain syntheses which assists the hypothesis of Atomic Form, are those of certain derivatives of Benzene. *Trimethyl Benzene* 1. 3. 5 or *mesitylene,* can be produced from three molecules of Acetone on treatment with sulphuric acid.
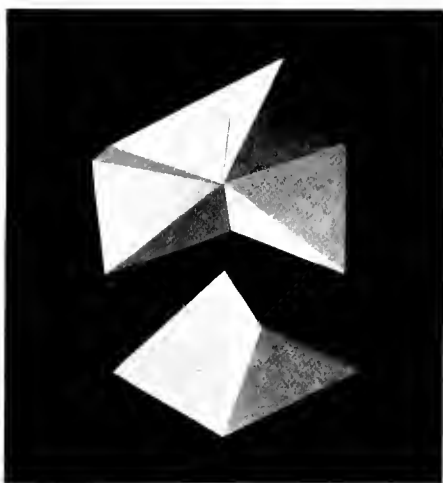
Acetone

$$\begin{array}{c} H \quad O \quad H \\ | \quad\; | \quad\; | \\ H-C-C-C-H \\ | \quad\; | \quad\; | \\ H \quad\quad H \end{array}$$

less $H_2O=$

$$\begin{array}{c} H \\ | \quad\; | \quad\; | \\ H-C-C-C-H \\ | \quad\; | \quad\; | \\ \quad\quad H \end{array}$$

three molecules of which when
nascent give

mesitylene

The model of the Carbon Framework of mesitylene, and the condensation of 3 Acetone molecules to produce Mesitylene, are shewn in Figs. 17 and 18, p. 25a, and it will be seen that its configuration is such that the three molecules of Acetone unite together so as to produce the Benzene Derivative without any change in the position of the carbons, or any break of the carbon framework. Any chain consisting of cubes or spheres or similar bodies would have to have a configuration $O-\overset{\overset{\displaystyle O}{|}}{O}$, or else the position of the carbon atoms would have to be changed, and the chain broken in order to enable the Benzene nucleus to be formed. The chain of Carbonoids in Acetone is so formed as to be able (after the loss of H_2O) to form one-third of the Benzene Derivative without any alteration.
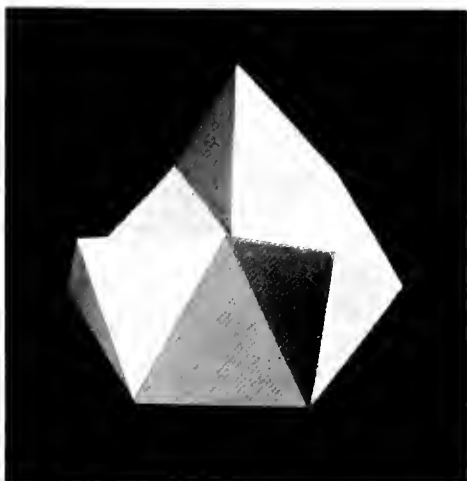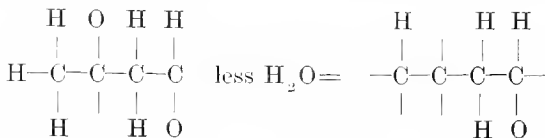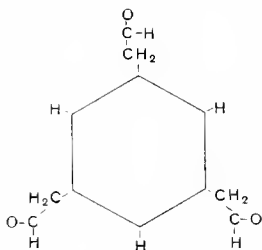
MESITYLENE
Fig. 17

Union of 3 ACETONE MOLECULES to form MESITYLENE
Fig. 18

A similar case is that of the synthesis of *Triacetyl Benzene* 1. 3. 5. from three molecules of *Aceto-acet-aldehyde*.
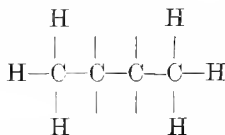

three molecules of which make
*Triacetyl Benzene* 1. 3. 5.

In this case the models shew that the Benzene Derivative is formed without bending or breaking the Carbon Chain.
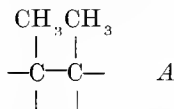
Again, three molecules of *Dimethyl Acetylene*

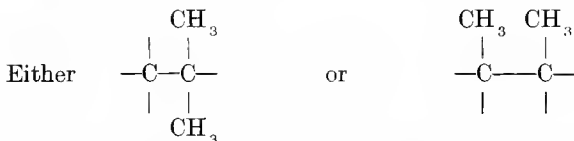will produce *Hexamethyl Benzene*.
C

In this case the molecule of the Dimethyl Acetylene must be of such a form that the atoms of $C.H_3$ will appear on the same side of the Benzene nucleus, thus :

$$C_{12} \quad H_{18}$$
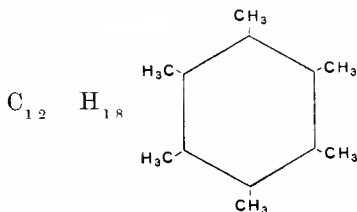
Dimethyl Acetylene must therefore have the form

$$
\begin{array}{cc}
CH_3 & CH_3 \\
| & | \\
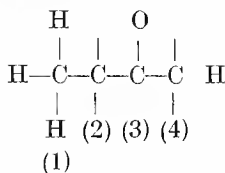-C-C- & \quad A \\
| & |
\end{array}
$$

The two CH_3 groups are evidently added to the opposite ends of the Acetylene group. There are two ways in which two single carbonoids can be added to an Ethyloid.

Either
$$
\begin{array}{c}
CH_3 \\
| \\
-C-C- \\
| \; | \\
CH_3
\end{array}
$$
or
$$
\begin{array}{c}
CH_3 \;\; CH_3 \\
| \quad | \\
-C---C- \\
| \quad |
\end{array}
$$

One is as likely as the other. We are, therefore, entitled to select the formula, the carbon framework of which is given above, A.

Three of these molecules can readily combine to form a Benzene Nucleus plus six groups of $C.H_3$ on the same side of the ring as already shewn above, without any change in the configuration of the carbon chain or any breaking of the chain.

Another interesting case of a similar character is the condensation of di-acetyl to form p. xyloquinone. On removing one molecule of water from each molecule of di-acetyl we have

$$
\begin{array}{ccccc}
\text{H} & & \text{O} & \\
| & | & | & | \\
\text{H—C—C—C—C} & & \text{H} \\
| & | & | \\
\text{H} & (2) & (3) & (4) \\
(1) &
\end{array}
$$

Here the three carbonoids Nos. (2), (3) and (4) are so arranged that they form one-half of a Benzene ring presenting a *co-planar* face consisting of one face of each of the two carbonoids C(2) and C(4) see Fig. 45, p. 72a. On removal of H_2O these co-planar faces are unsaturated and immediately unite to form

p.zyloquinone
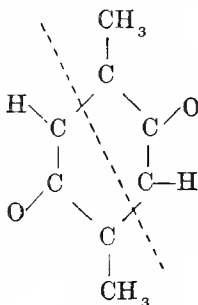
Here again the models shew a remarkable facility for the formation of the Benzene derivative.
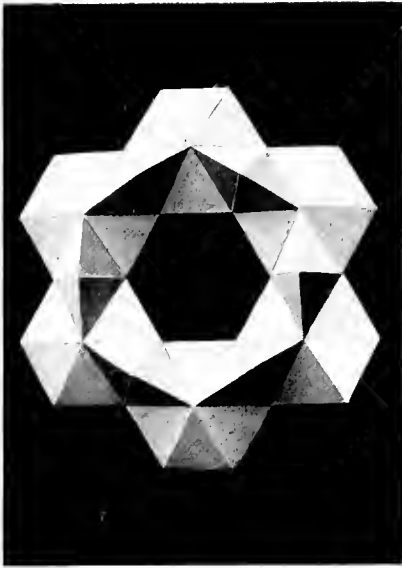
Fig. 19

Ring of 60 carbonoids, or 6 rings of 6 carbonoids
each, and 6 links of 4 carbonoids each.

CHAPTER IV.

THE ALLOTROPIC FORMS OF SOLID CARBON

Pure Carbon exists in three forms : Diamond, Graphite, and Amorphous Carbon. The production of amorphous carbon proceeds on the following lines. If Benzene is passed through a glowing tube Naphthalene $C_{10} H_8$ and Pyrene $C_{14} H_{10}$ are produced.

On heating Naphthalene or Pyrene to a *still higher temperature*, in absence of air, amorphous carbon results.

What number of carbon atoms are there in amorphous carbon and what is the form of the molecule ? There is strong ground for concluding that there are several rings of six carbons and that there is a large number of carbon atoms in the molecule.

In Fig. 19 we shew a ring of 60 carbonoids which is capable of indefinite extension and which may very well stand for a molecule of amorphous carbon.

When a lamp smokes the air is filled with little specks of amorphous carbon each of which will be made up of many thousands of these groups loosely held together. If, however, pure Carbon is formed under suitable conditions Graphite may be produced, but very high temperature and great pressure is needed to produce the Diamond. It is doubtful if Graphite can be considered as crystalline in formation, but it has *some* of the characteristics of a crystal.

If the structure here shewn is extended in all directions, a network is formed as shewn in Fig. 20, and this network may, under suitable conditions, extend in all directions in the same plane. Such a network may be fractured, and the line of fracture will be as shewn by the black lines on the figure. It will be seen that the lines of fracture form equilateral triangles.

Now let us look at a photograph of a piece of Graphite as seen through the microscope, Fig. 21, p. 30b. There are a number of lines clearly marked, and it is clear that these lines are all arranged relatively in the same way as the sides of an equilateral triangle. It is suggested that they represent the lines of fracture of a network of carbonoids as shewn in Fig. 20.

In support of this statement we may refer to the synthesis of Mellitic Acid by the oxidation of graphite or wood charcoal. Assuming that Graphite has the structure shewn in Fig. 20, viz.,
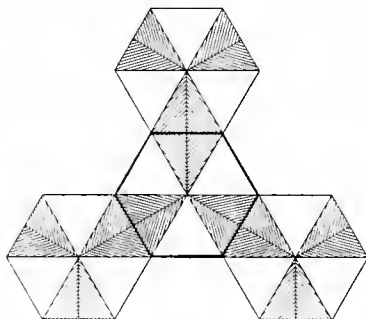
the lines of cleavage will be as shewn by the heavy line giving molecules of the following type and *leaving no residue.*
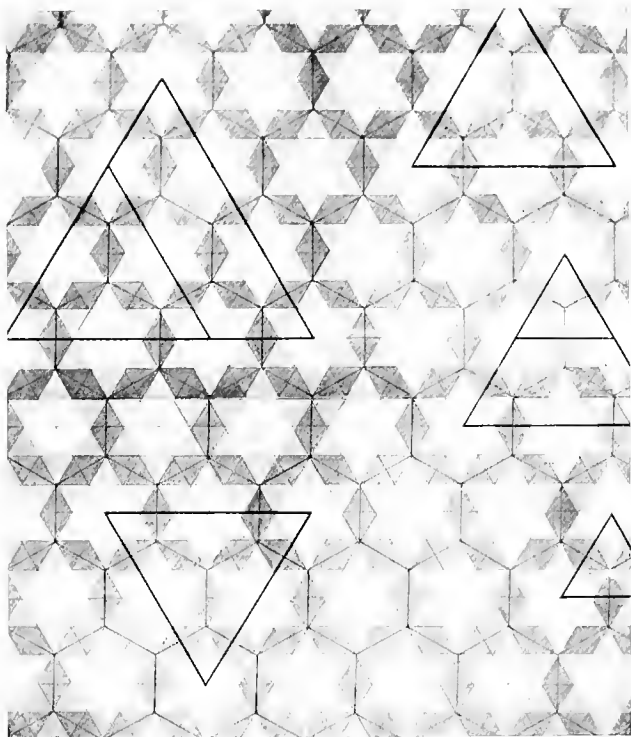
Fig. 20

Network consisting of the extension in all directions in
the same plane of the Rings of 60 carbonoids, showing
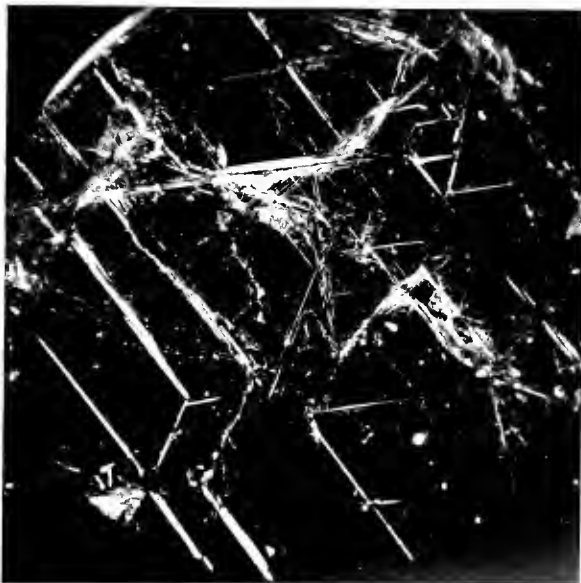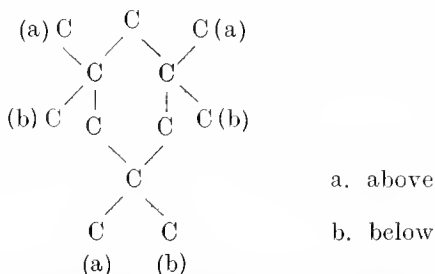the Lines of Cleavage.

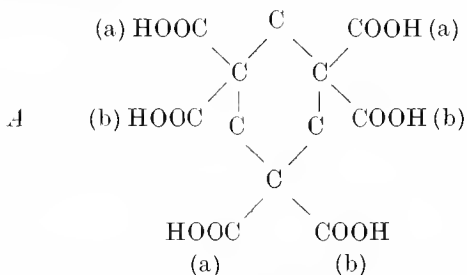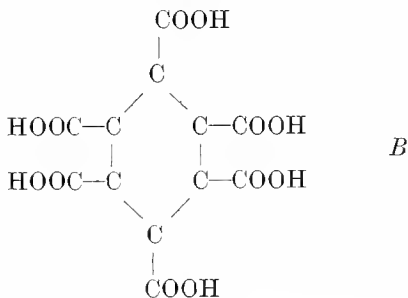Fig. No. 21
GRAPHITE.   Objective 1″

a. above

b. below

This accords with the assumed character of the carbonoid network, and would give the following formula for mellitic acid.

A

The usual formula for Mellitic Acid is

B

We have not been able to ascertain the evidence on which this formula is assigned to Mellitic Acid, and it seems possible that formula " A " may be correct.

There are other facts associated with the reactions connected with Mellitic Acid which indicate the probability that formula " A " is preferable to formula B. If this be the case, the form of the carbonoid network shewn in Fig. 20, p. 30a is confirmed.

The Diamond crystallizes in the form of a regular Octahedron or more rarely the cube, but these are compound figures. The simplest form of the Diamond is a tetrahedron, not the irregular tetrahedron of the carbonoid, but one that could be used for either an octahedron or a cube; the base is an equilateral triangle, and the three other sides are right-angled triangles.

If a few models of the tetrahedral form are made, they can be combined so as to form both the octahedron or the cube, and it will be seen that the three sides surrounding the apex of the tetrahedron will correspond with one half of the sides of the cube, the apex being the corner of the cube; and they will present an arrangement of squares while the base of the tetrahedron will present the appearance of equilateral triangles, and will correspond with the faces of the octahedron. Uncut stones are obtainable in all three forms, the tetrahedron, the cube and the octahedron.

The base of the tetrahedron and the faces of the octahedron are adorned with equilateral triangles representing the positions where a layer of the substance of the Diamond ends. Some photographs of the appearance of the face of the natural Diamond

Fig. 22
Face of CUBIC DIAMOND.   Objective 1″

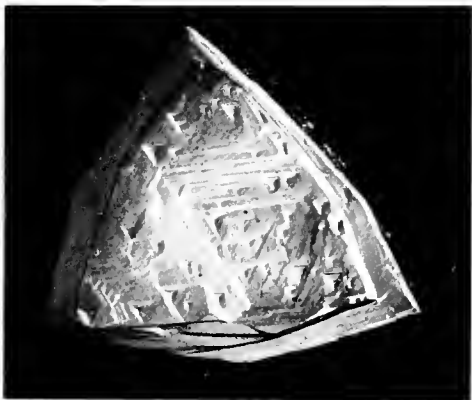
Fig. 23
A portion of Face of CUBIC DIAMOND.   Objective ¼″
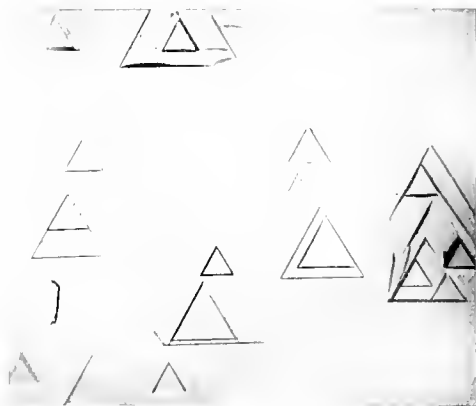
32a

Fig. 24
DIAMOND.
Base of TETRAHEDRON. Objective 1″

Fig. 25
DIAMOND.
Face of OCTAHEDRON. Objective ¼″

are now given, Figs. 22 and 23, and 24 and 25, and we see here the same formation which we saw in the case of graphite clearly portrayed.

It will be seen in Fig. No. 24 that the equilateral triangles are arranged in a position opposite to that of the triangular face of which they form a part, the bases of the triangles of the fractural markings being in the direction of the apex of the triangular face. If, however, the face of the Diamond be exposed to a high temperature under the oxyhydrogen blow-pipe, a portion of the surface is removed and a new set of equilateral triangles appears with their bases inverted so as to correspond in position with the triangular face of which they form a part.

On reference to Fig. No. 20, p. 30a it will be seen that the lines of fracture can be drawn in two different ways, either base above or base below, in this respect therefore the network of carbonoids is able to depict the natural phenomenon exhibited by the faces of the Diamond.

Dr Max Bauer, writing on the structure of the Diamond, says :

> " The Triangular pits are regular pyramidal depressions of which the bases are equilateral triangles. They are usually small and often only to be seen distinctly under the microscope. . . .
>
> " These depressions are of the same general character as those produced on the octahedral faces of a diamond during its combustion ; but while the *corners* of the pits of natural origin are adjacent to the octahedral edges, this position is occupied by the *sides* of the pits produced by etching, thus the two positions are the reverse of each

other. The pits occur singly or in large numbers, and the striations may or may not be also present on the same face."[1]

So far we have only arranged the carbonoids so as to produce a network with equiangular lines of fracture. Can a space-lattice be built up to correspond with the structure of the Diamond ? This can be done, but the number of carbonoids employed is so enormous that we have been compelled to resort to the use of hexagonal cards to represent the Benzene nucleus. In this way a model has been prepared which corresponds with the form of the tetrahedral Diamond. It will, however, be very difficult to include a photograph of this model in the illustrations by reason of the large size of the model required to shew the tetrahedral figure and the enormous number of cards which are required for its construction.

It is claimed that the capacity of the carbonoid to build up models of all the forms of solid carbon has now been shewn, but the illustrations fail to display fully the agreement between the models and the different forms of Diamond ; this can best be seen by consulting the models themselves.

NOTE.—27th January, 1922.

At the meeting of the British Association in Edinburgh, September, 1921, a Discussion took place on the Structure of Molecules—opened by Dr. Irving Langmuir. In the discussion which followed, Prof.

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[1] *Precious Stones,* Max Bauer, 1904, page 124.

W. L. Bragg, after considering the structural form of Calcium Carbonate as revealed by X-ray analysis, is reported to have said :

> " The interpretation of the Structure of Graphite is not quite so certain as that of calcite, but the evidence is very strongly in favour of a *hexagonal arrangement in sheets.*

> " Each carbon atom is equally related to three neighbours in the same plane. They are separated by a much greater distance from the atoms in other planes, and the cleavage indicates that the forces between successive planes are slight. These hexagons might be written as Benzene Rings with Valency Bonds, but such a formula would indicate a lowered symmetry of the structure, which is not the case."

CHAPTER V.

LAW OF EVEN NUMBERS.

The ordinary features of carbon chains are faithfully reproduced by the models; the well known formula C_nH_{2n+2} applies to strings of carbonoids, the available faces corresponding to $2n+2$.

We have already considered the Ethyloid with six faces. If to this one carbonoid be added the next group of three carbonoids has eight faces, and so on.

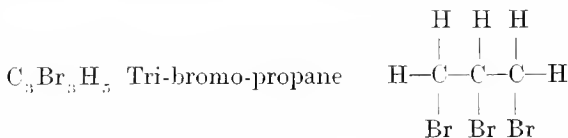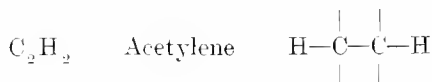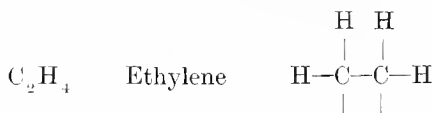The models serve equally well for representing the carbon framework of molecules with branched chains.

The number of Hydrogen atoms or its substituents attached to a carbon chain is always *even*, in the saturated compounds C_nH_{2n+2} the number of Hydrogen atoms is naturally even, and in the unsaturated substances with the formulæ C_nH_{2n} or C_nH_{2n-2}, the number of Hydrogen atoms is still even ; when other elements such as Halogens, Nitrogen, etc., are introduced into the molecule by substitution the total carbon valencies occupied remains an even number. From this it follows that the unoccupied carbon valencies are always 2 or a multiple of 2.

This peculiarity of carbon chains is thus described in Holleman's Organic Chemistry[1] " *Law of the Even Number of Atoms.*" The number of Hydrogen
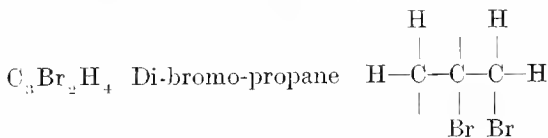
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[1] Holleman's Text Book of Organic Chemistry, 5th English Edition, pp. 47-48.

atoms in the saturated hydrocarbons is even, since their formula is C_nH_{2n+2}. All other organic compounds may be regarded as derived by exchange of these Hydrogen atoms for other elements or groups of atoms, or by the removal of an even number of hydrogen atoms or by both causes simultaneously. From this it follows that the sum of the atoms with uneven valency (Hydrogen, the Halogens, Nitrogen, Phosphorus, etc.), must always be an even number. The molecule of a substance of the empirical composition $C_3H_2O_2N$ must be at least twice as great as this, because $2H+1N$ is uneven."
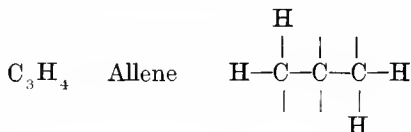
The following instances may be quoted :—

C_2H_4 Ethylene

$$H-\overset{\displaystyle \overset{H}{|}}{C}-\overset{\displaystyle \overset{H}{|}}{C}-H$$

C_2H_2 Acetylene

$$H-\overset{|}{C}-\overset{|}{C}-H$$

$C_3Br_3H_5$ Tri-bromo-propane

$$H-\overset{\displaystyle \overset{H}{|}}{\underset{\displaystyle \underset{Br}{|}}{C}}-\overset{\displaystyle \overset{H}{|}}{\underset{\displaystyle \underset{Br}{|}}{C}}-\overset{\displaystyle \overset{H}{|}}{\underset{\displaystyle \underset{Br}{|}}{C}}-H$$

on removal of H Br we get

$C_3Br_2H_4$ Di-bromo-propane

$$H-\overset{\displaystyle \overset{H}{|}}{C}-\overset{|}{\underset{\displaystyle \underset{Br}{|}}{C}}-\overset{\displaystyle \overset{H}{|}}{\underset{\displaystyle \underset{Br}{|}}{C}}-H$$

on removal of 2Br there remains

$$C_3H_4 \quad \text{Allene} \quad \begin{array}{c} \text{H} \\ | \quad | \quad | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ | \quad | \quad | \\ \text{H} \end{array}$$

If an attempt be made to satisfy the unoccupied valencies shewn, the molecule will take up Hydrogen, Chlorine, Bromine, Iodine, Oxygen, or other atoms, but so as *not to leave an uneven number of faces vacant.*

This Law is due mainly to the character of the carbon chain, and must be attributed to some peculiarity of its configuration. No satisfactory explanation has, hitherto, been put forward.

We will presently consider the three pairs of faces exhibited by the Ethyloid. A similar arrangement of pairs of faces exists in the Tri-carbonoid and all the compounds represented by higher numbers of carbonoids.

A photograph of a chain of 17 carbonoids, is here given and the arrangement of the faces *in pairs* may be easily seen ; see Fig. 26. The following characteristics should be noted :—

(1). The number of faces available is 36. (2n+2).

(2). The whole of these faces are arranged in pairs, viz :
      16 co-basal pairs and 2 pairs at each extremity
      of the chain. In this case the pairs (except
      the two pairs at the extremities) belong to
      adjacent carbonoids.

Fig. 26

CHAIN OF CARBONOIDS

A co-basal face is one in which the bases
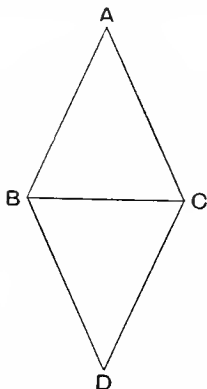of the two isosceles triangles are united ; thus :—

Fig. 27
Pair of Co-Basal Faces
Base B—C

(3). The faces may also be arranged differently according
to pairs of *concave* faces, there being 15 concavities
of two faces each = 30, + 3 odd faces at each
extremity of the chain. These pairs (excepting the
three at each extremity) belong to *alternate* car-
bonoids 1-3, 2-4, 3-5, etc.

(4). The two pairs of faces at each end of the chain
occupy special positions which correspond in all
respects to their fellows at the other end of the
molecule, they appear generally to retain their
attached atoms as in the cases of Acetylene and
Allene already mentioned. This may be due to
the fact that the attractive force at the two ends

of the chain will be greater than in the middle, as
it will operate most powerfully in the direction
of the longer axis.   Exceptions may be noted in the
case of Cyclo-Propane and other cyclic compounds.

The position of the pairs at the extremities of the
chain will be changed relatively to the rest of the chain,
and relatively to one another, as the number of car-
bonoids in the chain increases, and as we pass from odd
to even and even to odd, such changes of position will
be enhanced by any other atoms attached to these
faces as in the case of acids referred to in Chap. II.,
and they must affect materially the properties of the
molecule.   The addition of one carbonoid to the chain
has the effect of *reversing* approximately the direction
in which the pair of faces at the end of the chain is
pointing.

It is suggested that in all normal carbon chains, the
atoms of Hydrogen, etc., which are in attachment,
occupy the two sides of the co-basal pairs of faces,
and that the axis of rotation of the molecule will be
that which corresponds most nearly with the longer
axis of the chain.   Any increase in the rapidity of the
rotation will tend to throw off the attached atoms in
pairs, since if one element of the pair is removed the
stability of the other member of the pair will be simul-
taneously affected, in a similar manner, and to the same
extent, and will be removed at the same time.   The
effect of centrifugal force will be to drive the atoms
towards the solid angle separating the co-basal pair of
faces where they will meet, and further movement by
either atom should be retarded or stopped.   When the

rotation is enhanced and the centrifugal force becomes sufficiently strong, both atoms will be removed at the same time.

Similarly, in an atmosphere of nascent Hydrogen— if one side of the pair of faces is occupied, there will be created a position of stability on the other side of the solid angle which will be occupied by the nascent Hydrogen available, or failing such occupation, the single Hydrogen alone will be unable to retain its position.

It will be seen that the two co-basal faces belong to two *adjacent* carbonoids, thus agreeing with experimental data, and accounting for the phenomenon that when Halogens are removed from the molecule they take with them a Hydrogen atom from the *adjacent* carbon atom and not from the one to which the Halogen is attached. This peculiarity is shewn in the case of normal Propyl Iodide and Isopropyl Iodide, the models of which are shewn in Fig. 28, A. and B.
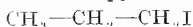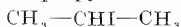
Normal Propyl Iodide   Isopropyl Iodide
CH_3—CH_2—CH_2I CH_3—CHI—CH_3
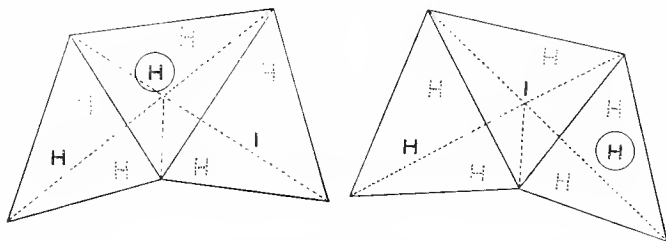A   B

Fig. 28

Note.   The letters in dotted lines, represent the atoms attached
to the remoter sides of the figure.

D

The Hydrogen which leaves the molecule along with the Halogen is enclosed in a ring, and the illustration shews that the Hydrogen is much more accessible to the attraction of the Iodine atom than the atom of Hydrogen on the *same* carbonoid which is at the other side of the molecule.

THE ETHYLOID

This Law of Even Numbers is well illustrated by the Ethyloid.   When Ethane is passed through a heated tube it loses two Hydrogen Atoms with the production of Ethylene C_2H_4.

The model of the Ethyloid presents three pairs of faces, one of which is a pair of co-basal faces, see Fig. 29.   The solid angle at B—C which divides these
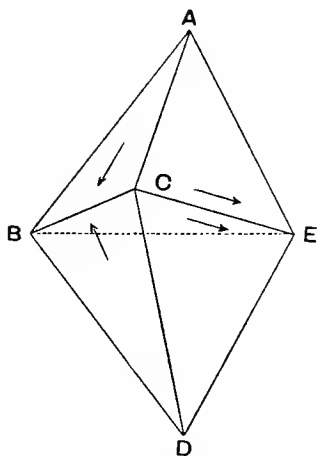

Fig. 29
Ethyloid

two faces occupies a medium position with regard to the Axis of Rotation and the two faces will have an equal retaining power on either side ; there will be no tendency to drive off an attached atom to the right or left ; see Fig. 29. The effect of centrifugal force upon any Hydrogen attached to these two faces will be to drive the two attached Hydrogen atoms towards the base B—C, where the force operating upon each of the two Hydrogen atoms being equal, and the directions opposite, they will meet and retard one another from further movement.

The effect of this (coupled with the position of the axis of rotation) will be that they will probably be the last to leave the molecule. This is important, as so long as this pair of Hydrogen is retained, the molecule is unable to join with other similar Ethyloids and produce a Benzene nucleus.

Of the other two pairs, they may be chosen in two ways—either two faces on the *same* carbonoid or two faces on the adjoining carbonoids. The latter seems the most probable, for the solid angle separating the pair of faces of adjoining carbonoids is very obtuse, while that separating the pair on the same carbonoid is acute. A reference to the model of the Ethyloid, Fig. 29, will shew that the two faces of the adjoining carbonoids are very close together. With regard to these two pairs of faces which are not co-basal, a careful study of the Ethyloid shews that the effect of centrifugal force upon an attached Hydrogen atom will probably be to drive it in the direction shewn by the arrows in figure Fig. 29 until it reaches the solid angle at A—E—D : this is an acute solid angle, where there will be little if any

obstruction to prevent it from passing off the Ethyloid.
The axis of rotation of the Ethyloid will no doubt be
determined by the position of its centre of gravity, and
will be nearer to the co-basal faces than it will be to
the other two pairs of faces, so that the point E,
(Fig. 29) will have a slightly more rapid movement than
the line B—C, and it will be the point where col-
lisions with other molecules will take place. If these
views are adopted we can see a reason why the Hydro-
gen attached to these two pairs of faces will be thrown
off by the increasing rotation of the molecule, in prefer-
ence to the Hydrogen attached to the pair of co-basal
faces.

These two pairs may be distinguished from each
other by the question of whether they lead or follow the
rotation of the Ethyloid. Whether the pair which
follows the Ethyloid will be more easily lost than the pair
which *leads* is a question on which there may be some
doubt, but it is clear that there will be a difference
between the two positions, and one pair will be cast off
more easily than the other. As the rapidity of the
rotation increases, it may be that one pair will be
liable to become detached by collisions with other
Ethyloids. In this way, Ethylene C_2H_4 will be pro-
duced.

On passing Ethylene through a red hot tube the
rapidity of the rotation of the molecule may be increased,
with the result that another pair of Hydrogen will be
lost, and Acetylene will result.

So far the removal of Hydrogen has not facilitated
the formation of a Benzene Ring, but on further treat-
ment with heat the last pair of Hydrogen is driven off

from the co-basal pair of faces and the Ethyloid unites with two other similar molecules to form a Benzenoid, thus :—
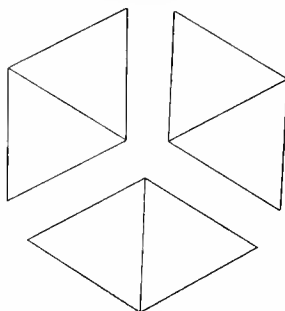

Fig. 30

It is interesting to observe that it is only on the removal of the last pair of Hydrogen Atoms that the formation of Benzene takes place, and that the peculiar formation of the Ethyloid seems to necessitate that the co-basal pair will be the last to leave the molecule.

Throughout it has been assumed that the Ethyloid has a rotational movement around an axis passing approximately through the centres of the two carbonoids. This seems to be inevitable. The Ethyloids, under the influence of a high temperature, must also have a translatory movement, and collisions will probably occur frequently. The effect of such collisions on a spherical body would be the production of a spin in one or both of the colliding molecules, and in the case of the Ethyloid it is difficult to conceive of a collision taking place without the production of a rotational movement in both molecules which will increase in rapidity with any rise in the temperature.

THE TRICARBONOID

The Tricarbonoid has 4 pairs of faces, two co-basal pairs, one on the front of the model and one on the back, marked A_1 and A_2, and B_1 and B_2. There is also one pair of opposite faces occupying the faces of the concave side marked C_1 and C_2, and a pair of single faces marked D_1 and D_2, occupying similar positions at the opposite ends of the figure. As shewn in Fig. 31.
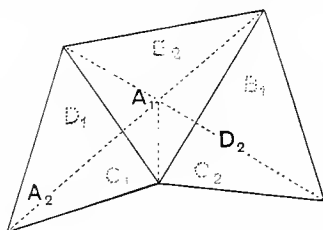

Fig. 31
The Tricarbonoid

The tetracarbonoid can be divided into pairs of faces in a similar way, and so on with other carbon chains.

THE BENZENOID

This figure cannot be divided into pairs of faces in the same way as the carbon chain. When Hydrogen is added to Benzene, the atoms are attached to the unsaturated faces of the Benzene nucleus *in pairs*. C_6H_8, C_6H_{10}, C_6H_{12}. See Holleman's Text Book of Organic Chemistry, First Edition p. 355.

" When the aromatic hydrocarbons take up two or four hydrogen atoms, they lose their aromatic

character and acquire properties peculiar to unsaturated compounds.

" *Dihydrobenzene*, C_6H_8, for example, reacts with a solution of permanganate and sodium carbonate, and also adds on four Bromine atoms.

" *Tetrahydro Benzene*, C_6H_{10}, readily adds on two Bromine atoms."

The special form of the Benzenoid and the comparatively smooth surface of its unoccupied side must render it very difficult for the first pair of Hydrogen atoms to become attached thereto, having regard to the fact that it must be considered as rotating rapidly around its shorter axis. When, however, one pair of Hydrogen or other atoms is attached, the smoothness of the surface would be disturbed and the addition of other atoms or groups would become comparatively easy. This may account for the change of character which takes place when addition products are made to Benzene and the fact that whenever it takes on two or four hydrogen atoms it acquires properties peculiar to unsaturated compounds.

Some doubt must still exist as to the cause of the adherence to linkage in pairs in these circumstances, but it is clear that the attachment of a single hydrogen atom would disturb the balance of the rotating Benzenoid, while the attachment of two Hydrogen atoms in opposing or balancing positions would preserve the equilibrium of the molecule. This phenomenon may also be considered as due to the character of the Hydro-

gen atom.   The Gas molecule of Hydrogen when it is
shaken apart to produce two atoms of nascent Hydrogen
may perhaps exist in a condition of partial separation,
so that the attachment of one atom involves the attach-
ment of the pair at the same time.   Until further
knowledge is obtained and the form of the Hydrogen
atom is known, the solution of this problem must
remain in abeyance.

CHAPTER VI.

TAUTOMERISM.

This phenomenon has received great attention from Organic Chemists and, under the title of " Dynamic Isomerism," has been the subject of a series of Reports to the British Association by a Committee presided over by Professor H. E. Armstrong.

The subject has been dealt with at some length by Cohen[1] in *Organic Chemistry for Advanced Students*, from which the following extract is taken.

" Since Laar drew attention to the subject in 1885, cases of tautomerism have rapidly multiplied. Before discussing the later development of this subject, a short account will be given of a few of the principal types of tautomeric compounds, that is to say, compounds which possess a double function, but are commonly represented by only one substance.

" If we examine the examples of tautomerism which have been given, we shall find that the structure of the compounds is such that it allows of the formation of isomers by the transference of a hydrogen atom from one polyvalent element to another, accompanied by a corresponding change in the

---

[1] Cohen—" *Organic Chemistry*," 2nd Edition, Part II. Structure, p. 318.

linkages. This structure depends, therefore, on the presence of certain groups.

" A convenient plan of classifying the greater number of tautomeric compounds has been proposed by Laar, who divides them into ' *Dyads* ' consisting of two polyvalent elements linked together, from one to the other of which the hydrogen atom may be supposed to travel ; ' *Triads* ' in which the original two polyvalent elements are separated by a third (which is of necessity at least tervalent) so that the hydrogen has now to travel from the first to the third element in the chain, and so forth."

After quoting a large number of cases of tautomerism, Cohen sums up the subject as follows[1]:—

" It will be seen that Laar's conception of one substance representing two structural isomers has not been consistently adhered to, for several cases are cited in which both isomers anticipated by theory are known. The latter have been called *Dynamic Isomers* sometimes or desmotropic compounds, to distinguish them from the single or tautomeric substance. Dynamic Isomers differ in no respect from ordinary Isomers but in the fact that they are more or less readily inter-convertible. . ."

" Fresh light has been thrown on the subject of tautomerism by the discovery of both structural forms of the familiar and peculiarly labile (Keto-enol) type of tautomeric compounds.

---

[1] Cohen—" *Organic Chemistry*," 2nd Edition, **Part II**. Structure, p. 330.

" Its immediate result has been to demonstrate the futility of the method hitherto adopted of attempting to ascertain the structural formula of a tautomeric compound from that of its derivatives or from the chemical behaviour of the compound itself.

" It has been shewn that the extreme mobility of one or both of the isomers renders them liable to isomeric change, not only in presence of a reagent, but frequently by a rise of temperature or the mere action of a solvent."

The Committee of the British Association referred to above in their Report state that Dynamic Isomerism includes all cases of reversible isomeric change and that it requires the aid of a catalyst to bring about the reaction. This is supplied by water or dust, and that the change is not an intramolecular one, but is the result of a complex heterogeneous molecular circuit.[1]

Without entering upon a discussion of any of the problems connected with this subject, we submit that when viewed from the standpoint of the theory of Atomic Form, cases of reversible Isomeric Change may be divided into three groups, namely :—

(1) CARBON CHAINS.

Transfers from Carbon to an adjacent Carbon or to an atom or group attached to an adjacent carbon atom.

(2). THE BENZENE NUCLEUS.

Transfers from attachment to one part of the Ring to another part, or to a group attached to some other part of the Ring.

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[1] Report of the British Association (1909), p. 137.

(3). TRIADS.

Transfers involving the passage of the labile Hydrogen from No. 1 to No. 3 in the carbon framework passing over No. 2.

In all these cases we deal only with transfers of position in which carbon, oxygen and hydrogen are concerned. Our ignorance of the probable form of Nitrogen and other elements renders it inadvisable to include transfers in which these atoms are involved.
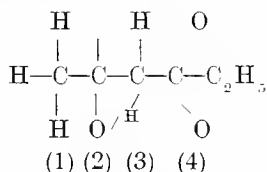
(1). CARBON CHAINS.

In the well-known example of aceto-acetic Ester, the two interchangeable forms are

$$CH_3—COH—CH—COO—C_2H_5$$

and

$$CH_3—CO—CH_2—COO—C_2H_5$$
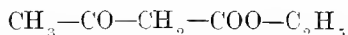
the labile Hydrogen may be represented as oscillating between the two positions, thus :—

$$
\begin{array}{cccc}
H & H & O & \\
| & | & | & \\
H—C—C—C—C—C_2H_5 \\
| & | & \nearrow H & \searrow \\
H & O & & O \\
(1) & (2) & (3) & (4)
\end{array}
$$

In a chain of four carbonoids there exist three co-basal pairs of faces, Nos. 1—2, 2—3, 3—4. In the pair 2—3, No. 2 carries an additional Oxygen Atom and the distance between a face of the Oxygen Atom and a face of No. 3 Carbon is quite small. It is not surprising if the attraction of the Oxygen attached to No. 2 is balanced by the attraction of Carbon No. 3, and in such a condition the Hydrogen might have a tendency to oscillate between the two positions.

Assuming for Oxygen an imaginary form of a tri-
angular Prism, with two faces equal to a face of the car-
bonoid, the position will be represented by one of the
following drawings :—
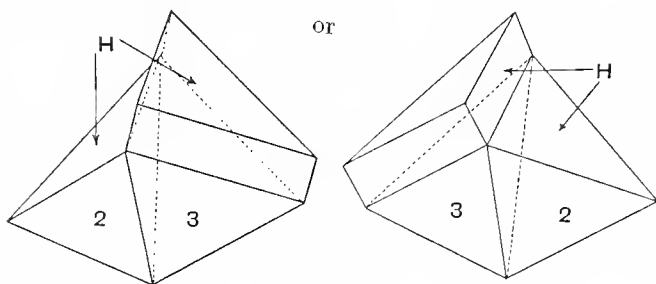
Fig. 32

One cannot suppose that the very light atom of
Hydrogen is tightly held by the attraction of the car-
bonoid, and when the temperature of the system is
raised and the rotation of the molecules increased, the
Hydrogen will momentarily leave its position in the
molecule, and on returning will, in some cases, attach
itself to the Oxygen.

Such an interchange seems very probable, even on
the assumption of spheres or cubes for the forms of
carbon and oxygen, thus :—
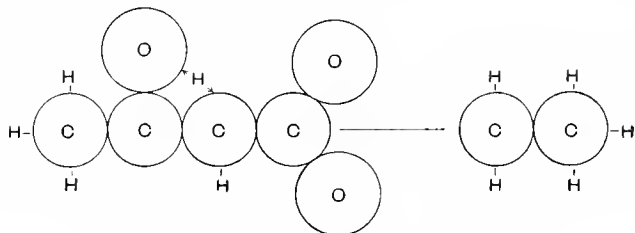
Fig. 33

(2). THE BENZENE NUCLEUS.

An example of this type of tautomerism is given by Professor Cohen.

NITROSO-PHENOL.   QUINONE-OXIME.
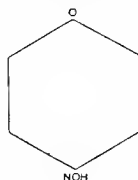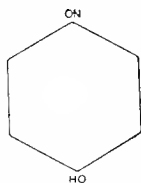
These formulæ represent the distance over which the Hydrogen atom travels to be the entire diameter of the Benzene Ring. On looking at the Benzenoid it is seen, however, that this is a comparatively short distance. See Fig. 34.
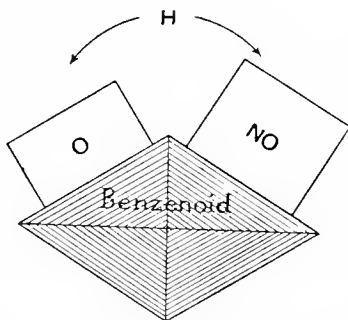

Fig. 34

The Oxygen and the Nitroso group will be in close proximity near the centre of the Benzene nucleus, and there is a strong probability of a Hydrogen atom being attracted from one to the other.

(3). TRIADS.

Examples of this type are numerous and include transfers from carbon to carbon and between the elements Carbon, Nitrogen and Oxygen. What the relative positions of the two atoms between which the Hydrogen is presumed to oscillate may be, we cannot tell, except where we have three carbons as in the following type.

$$\begin{array}{ccc} (1) & (2) & (3) \\ R\!-\!\!-\!\!-C\!-\!\!-\!\!-C\!-\!\!-\!\!-C\!-\!\!-\!\!-R \\ & \diagdown H \diagup \end{array}$$
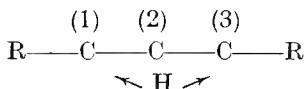
There are three ways in which three carbonoids may be arranged, viz :—

The right handed form,	either of these is repre-
The left handed form,	sented by Figs. 44 and
The straight form,	45, p. 72a.

In the first two of these forms there is a concavity separating one of the faces of No. 1 from one of the faces of No. 3, and a transfer of Hydrogen from one of these faces to the opposing face or to a group occupying the opposing face and *vice versa* could most easily be made. See Fig. 35, p. 56.

It will be seen that the intervening carbon, No. 2, occupies a position which entirely removes it from the field of action.
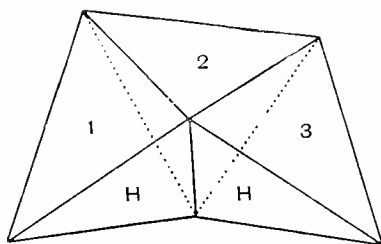
Fig. 35

In the case of an Oxygen atom occupying one of the faces of the concavity, the transfer of the Hydrogen atom becomes facilitated.

It is claimed that the existence of Tautomers of this type is a strong confirmation of the theory of Atomic Form, as only in chains of three or more tetrahedra, can an arrangement be made of such a type that the first and third of the tetrahedra are in close proximity and so readily suggest oscillation of the Hydrogen atom between the opposing faces.

This result may be achieved either intramolecularly or by a complex molecular circuit, for if the Hydrogen is entirely removed from the molecule to form part of a molecule of water or of some other chemical aggregate, and is then returned to the original molecule containing three carbon atoms, it would have the same opportunity of becoming attached to either side of the concavity.

Lapworth, in a paper on a possible basis of generalisation of Intramolecular Changes in Organic Compounds, states that the majority of reactions and changes

in Organic Chemistry, can be referred to necessary variations of one, or at most, two, simple laws, which find their most general forms in the relationship between, for example, the two forms of tautomeric and desmotropic substances, as for instance : $R_a M_1$. R_β : $R_\gamma M_2$ $\rightleftharpoons R_a$: R_β. $R_\gamma M_1 M_2$. $\rightleftharpoons R_a M_2$. R_β : $R_\gamma M_1$, and he suggests the following graphic representation to explain the transfer of M from No. 1 to No. 3.
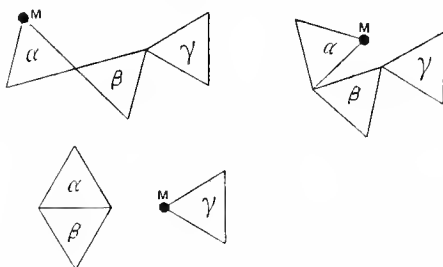
In this connection he suggests that it is not necessary to imagine that the group M ever actually becomes free, but rather that it is always under the influence of the attraction of R_a or R_γ, and possibly at some instant of both simultaneously, thus the labile character of the molecule may be imagined to depend upon a species of dissociation.[1]
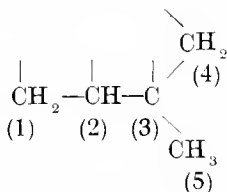
The graphic illustration shewn in the paper, of which a copy appears above, is evidently designed to shew how a labile atom may be transferred from No. 1 to No. 3 passing over No. 2. Transfers of this character are clearly provided for in all carbonoid groups, as already explained, see Fig. 35.

E

CHAPTER VII.

ISOPRENE AND RUBBER

The models may be used as a means of deciding which of two formulæ is to be considered as the correct one. As an instance, let us take the model of Isoprene, Fig. 36, p. 58a.

$$
\begin{array}{ccc}
& & \diagdown \\
& & \text{CH}_2 \\
\mid & \mid & \mid \diagup (4) \\
\text{CH}_2 - \text{CH} - \text{C} \\
(1) & (2) & (3) \diagdown \\
& & \text{CH}_3 \\
& & (5)
\end{array}
$$

At the Meeting of the British Association at York in 1906, W. A. Tilden reported on the polymerization of Isoprene; he then stated :—[1]

> " It appears probable that the slow polymeriza-
> tion which ultimately results in the production
> of solid India-rubber is due to a different mode
> of linkage, leading to the formation of long
> chains. Except on the assumption of a shifting of
> Hydrogen this can only take place on the condition
> of the formation of a series of tetramethylene rings."

[1] Brit. Assoc. Reports, York, (1906), p. 525.
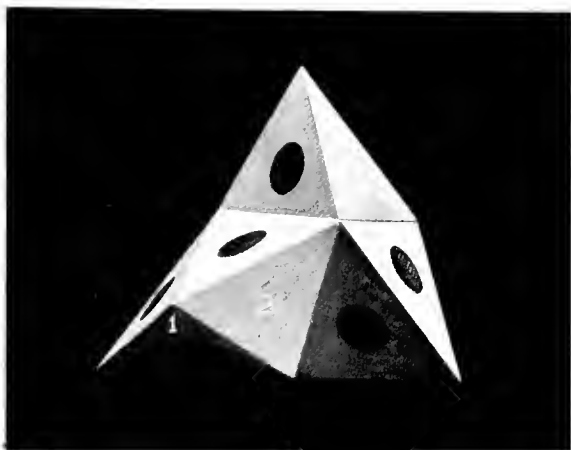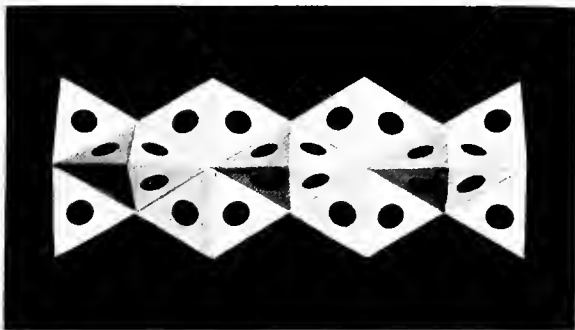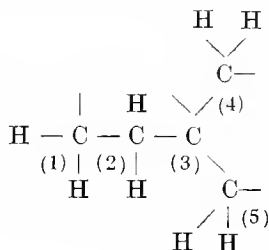
Fig 36
Model of Isoprene

Fig. 37
Chain of Carbon Atoms of indefinite length.

Note.—The black spots indicate the positions assumed to
be occupied by Hydrogen.

If a change takes place gradually in the position of the " H " atom so as to produce the following :—

$$
\begin{array}{c}
\text{H \quad H} \\
\diagdown \diagup \\
\text{C}- \\
| \qquad \text{H} \quad \diagdown \diagup (4) \\
\text{H} - \text{C} - \text{C} - \text{C} \\
(1) \, | \, (2) \, | \quad (3) \diagdown \\
\text{H} \quad \text{H} \qquad \text{C}- \\
\diagup \, | \, (5) \\
\text{H} \quad \text{H}
\end{array}
$$

the molecule will be of such a form that two pairs of co-planar faces would be presented, viz. : Nos. 1 and 3 and Nos. 4 and 5, and these would be available for linking to another molecule of Isoprene.

By reason of these two pairs of co-planar faces (see the annexed photograph, Fig. 36), molecules of this kind could form long chains or filaments of indefinite length, which would be marvellously fine and delicate, but as the carbon atoms will be held together by their mutual attractions only, they would always be capable of a slight separation at each joint in the carbon chain, the existence of an enormous number of such joints in a small piece of each filament would produce a power of stretching and recovery of a marked character.

The appearance of the chain of carbon atoms is shown in the photograph Fig. 37, and may be extended indefinitely.

Harries has put forward an eight membered ring formula.
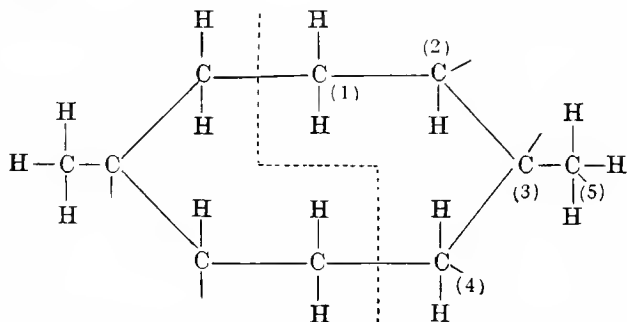
The carbon No. 4 in the formula of Isoprene.
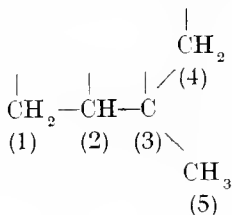
is assumed to form part of the eight membered ring, but our models shew that the three carbons (4), (3) and (5) form part of an independent ring.

They also shew that the unoccupied faces or unsaturated linkages of the CH_2 (1), CH (2) and C (3) are also part of another ring and that CH_2 (1) and C (3) form a co-planar pair of faces, C (3) being common to both rings, and that on the removal of one Hydrogen from CH_3 and the transference thereof to CH making it
                (5)   (2)

CH_2, the two atoms CH_2 and CH_2 form another co-
$\qquad\qquad\quad$ (4) $\qquad\quad$ (5)
planar face, both of which are available for linking to
another similar molecule.

It will thus be seen that before Isoprene can poly-
merize a change in the arrangement of the Hydrogen
is necessary. One of the Hydrogen atoms in CH_3 being
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (5)
removed to the unoccupied linkage of CH.
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (2)

In the above formula this appears to be a difficult
operation, as the Hydrogen would have to pass over C,
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (3)
but when the models are inspected, it is seen that these
atoms are adjacent, see Fig. No. 36, p. 58a, where the
relative positions of No. 2 and No. 5 are shewn. It will
thus be apparent that the shifting of Hydrogen men-
tioned by Prof. Tilden in 1906 can now be shewn to be
a probable occurrence.

Although CH_3 and CH are now shown to be adja-
$\qquad\quad$ (5) $\qquad\quad$ (2)
cent atoms, the two faces concerned in the necessary
transfer of Hydrogen are not *adjoining faces*, and it
appears to be necessary to pass over to the other side of
CH_3 in order to reach CH. This is not a difficult
(5) $\qquad\qquad\qquad\qquad\qquad$ (2)
transfer, but it is probable that it will not take place
immediately nor very readily ; this may be considered
to be consistent with the slow rate at which poly-
merization of Isoprene takes place.

It seems highly probable that gradually the juxta-position of another molecule with a co-planar face, free from Hydrogen, will cause the removal of a Hydrogen atom from the CH_3 group and its transference to CH.

$$(5) \qquad\qquad (2)$$

When this change takes place, the polymerization of Isoprene will immediately follow, and if this be continued the long delicate filaments of caoutchouc will result. These filaments will not crystallize, but lying in close contact extending in all directions would constitute a highly elastic solid, provided we may assume that the property of elasticity possessed by India-rubber is due to the stretching and recoil of these filaments.

Pickles, in a paper read before the Chemical Society of London in 1910[1], suggested that the unsaturated nuclei C_5H_8 of Isoprene might unite to form long chains of the following structure:

$$...CH_2 \cdot \overset{\overset{\displaystyle Me}{\displaystyle |}}{C} : CH \cdot (CH_2)_2 \cdot \overset{\overset{\displaystyle Me}{\displaystyle |}}{C} : CH \cdot (CH_2)_2 \cdot \overset{\overset{\displaystyle Me}{\displaystyle |}}{C} : CH \cdot (CH_2)_2...$$

and that the number of C_5H_8 complexes involved in the chain might vary in different kinds of Rubber. His formula for Isoprene is

$$
\begin{array}{cccc}
| & | & | & | \\
H-C-C-C-C-H \\
| & | & | & | \\
H & & H & H \\
H-C-H \\
| \\
H
\end{array}
$$

[1] "*Journal of the Chemical Society,*" Vol. XCVII. p. 1085, (1910).

and he shews grounds for rejecting the eight membered ring proposed by Harries.

Models can be prepared in accordance with Pickles' formula, but they are not of a compact or symmetrical form, and the chains would be of two kinds, right and left handed and involving optical activity (see Chapter IX.). We think that the carbonoid chain shewn in Fig. 37, p. 58a, is the most probable explanation of the structure of rubber, although it involves a change in the position of one Hydrogen atom.

In Stewart's *Recent Advances in Organic Chemistry*,[1] the subject of Natural and Artificial Rubber and the various syntheses of the artificial product are fully considered, and it appears that normal rubber can be prepared from Isoprene, by the formation of an intermediate product called β. Myrcene $C_{10}H_{16}$, resulting from keeping Isoprene at a temperature of 80°—90°. This dimeric form is subsequently treated with Sodium for the production of Normal Rubber.

From what has been already stated with regard to the model of Isoprene it will be seen that each molecule has one co-planar face, (Nos. 1 and 3 in the above formula), available for linkage to another molecule of Isoprene without any change in the arrangement of the attached Hydrogen, so that when the substance is submitted to a moderate temperature the β. Myrcene compound is formed.

The further polymerization requires the assistance of Sodium, and a change in the position of one of the Hydrogen atoms as above explained.

[1] Stewart—" *Recent Advances in Organic Chemistry*," (1920), p. 103-116.

Even if the reader is unable to accept the Scheme of Atomic Form he will find that the use of models will in this case assist him in the consideration of the formulæ, and by shewing the existence of pairs of co-planar faces (Nos. 1—3 and Nos. 4—5) will enable the formation of a filament to be more easily apprehended.

CHAPTER VIII.

TRIPHENYL-METHANE.

$$(C_6H_5)_3 \text{ CH or } C_{19}H_{16}.$$
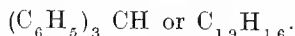
Some attention should be given to this compound on account of its theoretical importance. The group $(C_6H_5)_3$, or $(C_6H_4)_3$ combine with Nitrogen and other groups, occupies an unique position in the molecule of many important Chemical Dyes, including the rosanilines. It also polymerizes to form Hexaphenylethane $(C_6H_5)_3 \text{ C---C } (C_6H_5)_3$.

Consideration of the models indicates that while it may be possible to arrange three Benzenoids around a single Carbonoid, the arrangement is not symmetrical and the resulting model of the Triphenyl-methane molecule is not at all likely to be stable.

The arrangement of three Benzenoids around one Carbonoid is suggested by the formula, the idea evidently being that one Hydrogen must be omitted from each Benzene Ring, so as to allow of a linkage to the single carbon which is supposed to be situated in the centre of the molecule, the remaining affinity being represented by the single Hydrogen attached to the central carbon. The compound was thus made to appear to be saturated, except for the normal unsaturation of the Benzene Rings.

For a long time, it appeared that this was one of the most difficult cases, arising in connection with the

Theory of Atomic Form. Further consideration, however, shews that the method of arrangement shewn in Fig. 38 may be adopted.

In the synthesis of Triphenyl-methane, Benzene takes an important part, as shewn below.

$$(C_6H_5)\,C\overset{\displaystyle H}{\underset{\displaystyle O}{\Big\langle}} + 2(C_6H_6) = (C_6H_5)_3CH + H_2O$$

$$(C_6H_5)CH{-}Cl_2 + 2(C_6H_6) = (C_6H_5)_3CH + 2HCl$$

$$CHCl_3 + 3(C_6H_6) = (C_6H_5)_3CH + 3HCl$$
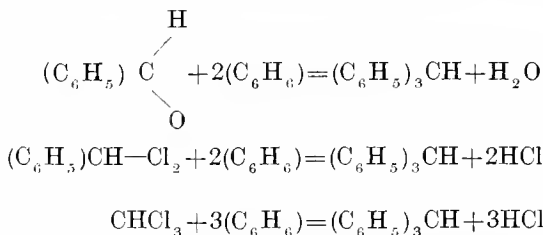
It is true that the Hydrogen may be supposed to retain its place in attachment to the single carbon and that each of the Benzene Rings may give up one Hydrogen, but it may equally well be the case that only one Hydrogen is taken from Benzene and one from the attached Carbonoid, or that the single carbon takes on an additional Hydrogen, making CH_2 leaving one of the Benzene Rings with only four, but it seems reasonable to adopt the scheme by which the extra Carbonoid is attached to the Triphenyl group, and does not constitute the centre of the molecule. It is introduced into the molecule in attachment to one Benzene Ring, and the molecule is completed by the association of two additional Rings. In doing so they may each give up one Hydrogen in order to complete the molecule of Water or Hydrochloric Acid, without becoming directly attached to the single Carbon.
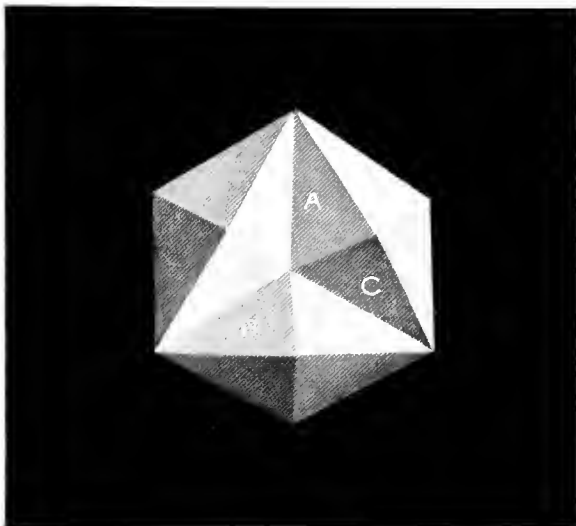
Fig. 38
Tri-phenyl Methane.
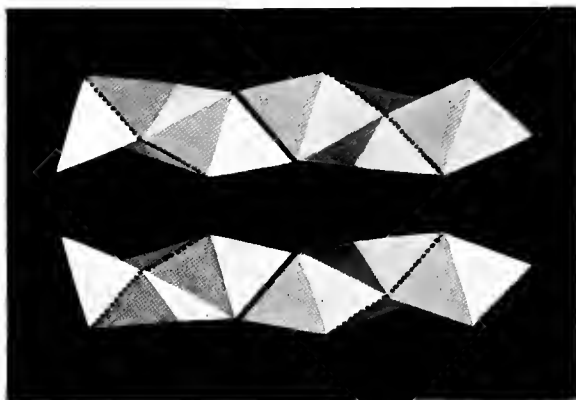
Fig. 43 (See p. 74).
Right- and left-handed Spirals.
Asymmetric arrangement of the Carbonoid Chain.

66a

It must be remembered that the Phenyl group has one side entirely unsaturated and therefore available for attachment to other Rings. Three Benzenoids have therefore three sides which can be brought into contact free from any hindrance caused by attached Hydrogen. The unsaturated sides of the Benzenoid have each two faces which can be arranged so as to form attachments to other Benzenoids.

The form of the Benzenoid is such that a new complex is thus formed of a compact and stable configuration, a photograph of which is shewn in Fig. 38.

To a molecule of this configuration a carbon atom may be attached in such a way as to produce a co-basal and co-planar pair of faces, available for union with any other molecule of Triphenyl-methane or with other groups.

In order to express the arrangement of the carbonoids in this molecule a special type of notation will be used viz. :

BENZENOID.
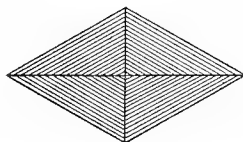
Fig. 40

View from the side of the molecule.

The Tri-phenyl Group $(C_6H_5)_3$ will be indicated thus :—

C_{18}
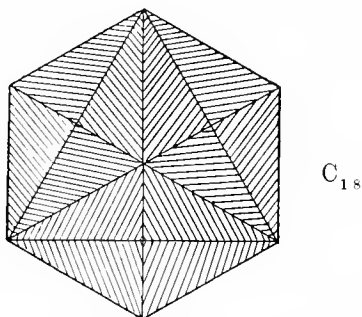
Fig. 41

The Hydrogen may be arranged in three different ways :—

I.	II.	III.
C_6H_5 C_6H_5	C_6H_6 C_6H_5	C_6H_4 C_6H_5
$C_6\|H_6$	$C_6\|H_6$	$C_6\|H_5$
CH	C	CH_2
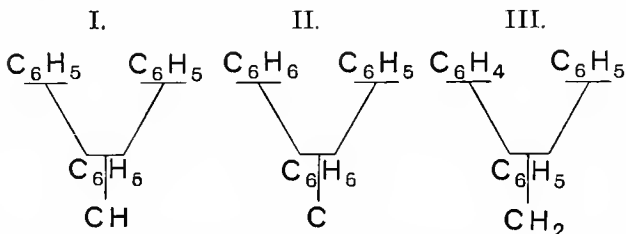
In all three of these arrangements there will be four unsaturated faces distributed between the C_6H_5 groups and the single carbonoid. In each arrangement there will be a co-planar face between C_6H_5 and CH or CH_2, respectively, and in No. III there will be, in addition, two single unsaturated faces on the opposite side of the molecule (C_6H_4) and in No. 1, one such face. The

unsaturated condition of the group corresponds to the molecule's remarkable power of forming addition products with ether and many other compounds and the readiness with which oxidation takes place.

A complete double molecule of Triphenyl-methane will be represented thus :—

$$(C_{19}H_{16})_2$$
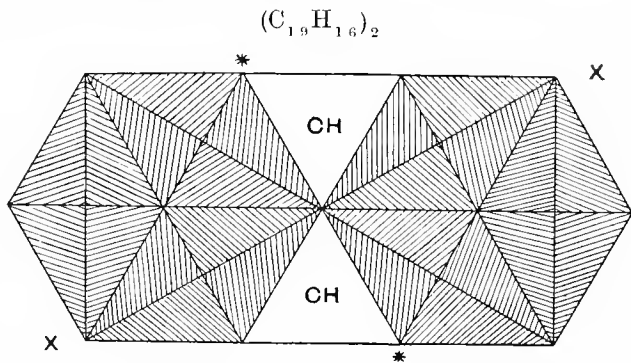
Fig. 42

The co-planar faces extend from * to *
The unsaturated faces are situated at x

It will be seen that the double molecule is capable of further attachment to other atoms or groups. The model shews that for each *single* molecule there is one unsaturated face on the opposite side of the phenyl group as well as a coplanar face, and a vacant face on the back of the methyl group CH. If the methyl has two Hydrogen in attachment, there will be two faces vacant on the opposite side of the Tri-phenyl group, and this might enable a net-work to be built up which could be extended horizontally in all directions.

The double molecule above depicted corresponds to Hexaphenyl-ethane, the carbon linking in which can be so easily broken ; this is easily understood when the masses of the two triphenyl groups are considered and the fact that they are not directly linked together.

$$\text{In rosaniline} \quad HO-C \overset{\displaystyle C_6H_4NH_2}{\underset{\displaystyle C_6H_4NH_2}{\diagup}} C_6H_4NH_2$$
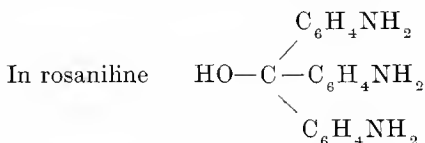
three amino groups are attached to the three phenyl groups and one hydroxyl group is attached to the additional carbon, but leaving the triphenyl group unaltered and leaving four unsaturated faces including the co-planar face already mentioned.

In rosaniline and other compounds containing amino groups, Oxygen, etc., the construction of a crystalline form is probably assisted by the attached groups and atoms.

The Triphenyl group is capable of carrying six atoms attached to the two opposing sides of two phenyl groups in the positions marked AA, BB and CC above and below in the foregoing illustration, Fig. 38, p. 66a. These faces, however, do not appear to be occupied. There would probably be difficulty in introducing a Carbonoid into these positions.

Although the theory of the constitution of Triphenyl-methane set forth above has some points in its favour, it is not free from difficulties. It is maintained by some chemists that Triphenyl-methane should be considered

as a methyl group, surrounded by three phenyl groups, all three being in contact with the central carbon. This view is supported by the fact that it can be synthesized from Benzene and chloroform and that one of the Hydrogen atoms, being in union with the central carbon, acts differently from all the others and on oxidation becomes reduced to —OH.

It must also be acknowledged that the Chemical evidence with regard to Triphenyl-methane points to the methyl group being an essential part of the molecule without which it could not exist. In the position which we have assigned to it in attachment to the outside of the Triphenyl group it could be dispensed with, leaving a group which we should expect to be able to isolate and to record its characteristics.

The constitution of Triphenyl-methane has been the subject of much speculation and controversy, and doubts exist as to whether the molecule is not a double one in the form of Hexaphenyl-ethane, although readily decomposed into Triphenyl-methyl in which form it recombines with other atoms and groups.

If this view is correct, the difficulties surrounding the constitution of the molecule would to a large extent disappear, since in Hexaphenyl-ethane the two carbon atoms are shewn to be in the centre of the group.

Whatever form is assigned to Carbon it is difficult to conceive of three Benzene rings (77 each), attracted and held by a single carbon atom in the centre of the molecule.

It is clear that the question of the constitution of Triphenyl-methane and Hexaphenyl-ethane is open to considerable doubt and must be reserved for further consideration. This subject is fully discussed in Stewart's "*Recent Advances in Organic Chemistry*," Chapter IX.[1] In the 5th section of this chapter he writes :—

> " We have now exhausted the possibilities of static formulæ to explain the behaviour of Tri-phenyl-methyl ; and it is evident that the results have not been completely satisfactory. All the three views which we have discussed in the foregoing sections have certain advantages ; and each has its own drawbacks. It thus becomes clear that, if we are to make any further progress towards a solution of the problem, we must contrive some means of uniting the advantages of the various formulæ ; while at the same time we must endeavour to minimise their weak points. In order to do this it is obvious that we must turn to modern dynamic ideas and represent Triphenyl-methyl as a series of equilibrium mixtures of isomerides. Gomberg has developed this line of thought : and if his results do not represent the truth, it seems probable that they come very close to it."

It is hoped that the suggestions put forward in this chapter may be of use in helping towards the solution of a problem of much complexity and difficulty.

[1]Stewart—" *Recent Advances in Organic Chemistry*," (1920), p. 295.
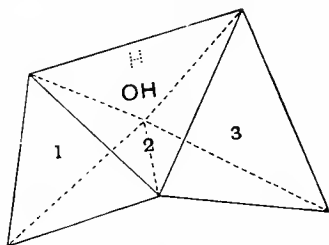
Fig. 44a
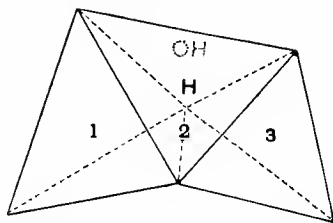
Fig. 44b

Fig. 45

Fig. 50

72a
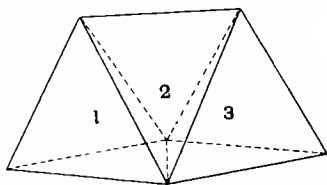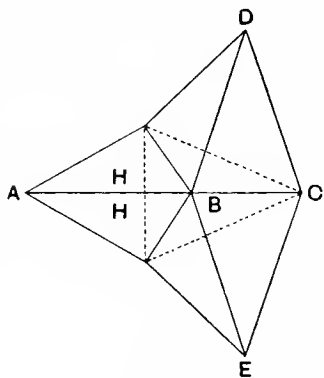
Models of the TETRACARBONOID

a   b
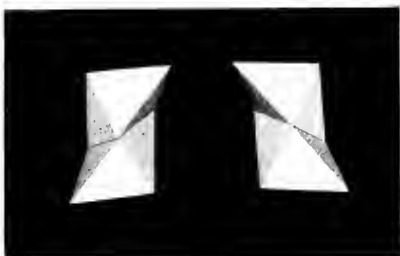
Fig. 46 OPTICAL ISOMERS.

a   b

Fig. 47 OPTICAL ISOMERS.
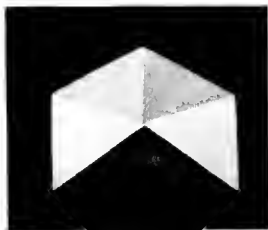
Fig. 48 INACTIVE FORMS.   Fig. 49

CHAPTER IX.

OPTICAL ACTIVITY OF CARBON COMPOUNDS.

In the year 1860, PASTEUR, by his researches on the Tartaric Acids, laid the foundation of Stereochemistry, and Van't Hoff[1] in 1898, quoted the following instructive passage from PASTEUR'S writings:—

> "Are the atoms of Tartaric Acid arranged along the spiral of a right-handed screw, or are they situated at the corners of an irregular tetrahedron, or have they some other asymmetric grouping? Time must answer the question. But of this there is no doubt, that the atoms possess an asymmetric arrangement like that of an object and its mirrored image. Equally certain is it that the atoms of the left-handed acid possess just the opposite asymmetric arrangement."

During the sixty years that have passed since these words were written, an enormous amount of study has been given to asymmetric Isomerism, and a mass of detail has been recorded; the subject is still, however, involved in much controversy and speculation, and many problems await solution.

---

[1] *"The Arrangement of Atoms in Space,"* 2nd Edition, p. 12, (1898), J. H. Van't Hoff.

F

Stewart, in *Stereochemistry*,[1] writes :—

" In the purely stereochemical field, much yet remains to be done in the examination of isomeric compounds for the existence of which no explanation can be adduced under current theories."

It is claimed for the theory of Atomic Form that right-handed and left-handed spirals are displayed by the carbonoid aggregates when arranged to represent carbon chains, resulting in an asymmetric arrangement like that of an object and its mirrored image. The two spirals are shewn in Fig. 43, p. 66a.

The Carbonoid itself is an *irregular* Tetrahedron, as suggested by Pasteur, and to its special configuration is due the asymmetry of the carbonoid chain and its power of depicting a large number of carbon compounds.

With the view of simplifying the discussion of the optical activity of carbon, it is proposed to omit all reference to stereoisomerism arising in compounds of other elements, such as Nitrogen, Silicon, Tin, Cobalt, etc.

While on one hand the current theories do not afford a satisfactory explanation of many facts connected with this branch of chemistry, the Theory of Atomic Form has no magic wand by which it can explain the complex problems involved. It is proposed to set out certain features of the theory bearing upon the subject and to await the extension of our knowledge and the result of further experimental research.

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[1] Stewart—" *Stereochemistry*," 2nd Edition, (1919), p. 240.

The Carbonoid Aggregates for two carbonoids only exist in one form, the " Ethyloid," but on proceeding to arrange *three* carbonoids there are three different forms available called " Tricarbonoids," drawings of which are shewn in Figures 44a and b, and Fig. 45, p. 72a.   The two Figs. 44a and 44b are mirror images of one another and cannot be superimposed.   They are the beginnings of the two spiral chains, the forms assumed by strings of carbonoids—such chains are in two forms, the spiral figure being directed round the chain in the form of a right-handed screw in one case and as a left-handed screw in the other, as will be clearly seen by the photograph of two chains of 17 carbonoids each, Fig. 43, p. 66a.

It is interesting to note that no compounds shewing optical activity have less than *three* carbon atoms in the molecule, with the exception of

<div align="center">

Chloro-iodo-methane sulphonic Acid

Cl
|
(a)—H—C—SO$_3$H—(b)
|
I
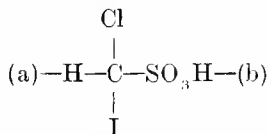
and Fluoro-chloro-bromo acetic Acid.

F
|
(a)—Cl—C—COOH—(b)
|
Br

</div>
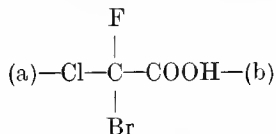
Both of which have been resolved into two optical isomers.[1]

---

[1] Stewart—" *Stereochemistry*," 2nd Edition, (1919), p. 11.

In the first case, if the central carbon is represented by a Sphere, it would be difficult to arrange the atoms so as to represent two right and left-handed Isomers, as the figure could be rotated around the axis a—b without altering its appearance, and any change in the relative positions of the Chlorine and Iodine atoms would be nullified by revolving the molecule in this way, the same would apply to the second case.   If however the central carbon has a tetrahedral form, it will be possible to exchange the positions of the Chlorine and Iodine in the first case, and the Fluorine and Bromine in the second case, thus producing in each case two isomers which will be mirror images of one another, and enantiomorphism will result.

Compounds of this type appear to belong to a different class from the optically active compounds of 3, 4 and 5 carbons which we are now considering.

It may therefore be stated that the Theory of Atomic Form agrees generally with the facts, in regard to the point at which the optical activity of carbon compounds commences.

A large number of Optical Isomers are known where it is clear that the isomerism is due to the transposition of an atom or group from one side to the other of the molecule, even in some cases where no asymmetric carbon atom is disclosed, such a compound is 1-methyl-cyclo-hexylidene 4-acetic acid.
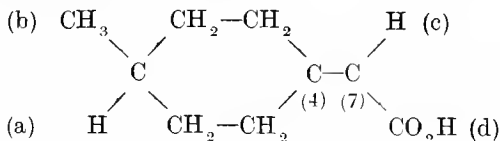
This substance is discussed in a paper read before Section B of the British Association at Portsmouth (1911), by Wm. H. Perkin and Wm. Jackson Pope.[1]

The synthesis was described and the substance resolved into its right- and left-handed isomers.

The writers of the paper decided that the groups marked (a) and (b) do not lie in the plane of the paper, but in a plane at right angles to the six carbon atoms forming the ring. Similarly the two carbons at the other end of the ring marked (4) and (7) are in the same plane as groups (a) and (b) but the two groups (c) and (d) are again in the same plane as the paper.

If a model is made of this molecule, using carbonoids to represent the carbon atoms, the form presented will shew all the features described above, and the right- and left-handed configurations due to the positions occupied by the groups (c) and (d) relatively to the rest of the molecule will be made evident. If the positions of H(c) and CO_2H(d) are interchanged, we get the mirror image of the original figure and the two optical isomers are produced.

The authors of the paper have described this configuration as " centro-asymmetric." They state that compounds of this type open up a wide field of enquiry.

It is submitted that—whatever view may be held with regard to the Theory of Atomic Form—it will be found that the use of models of carbonoids will facilitate the study of these more complicated compounds, and enable the position in the molecule of the various groups to be more readily understood.

[1] Brit. Assoc. Reports, Portsmouth, (1911), p. 361.

A simpler case is that of secondary Butyl-carbinol.

$$
\begin{array}{ccc}
\text{H} & \text{H} & \text{H} \\
| & | & | \\
\text{H—C——C——C—OH} \\
\text{(2)}\,| & | & |\,\text{(1)} \\
\text{H} & | & \text{H} \\
& \text{H—C—H} & \\
& | & \\
& \text{H—C—H} & \\
& | & \\
& \text{H} &
\end{array}
$$
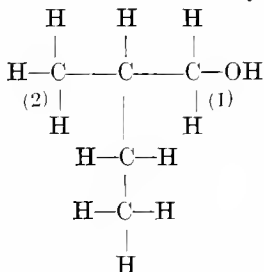
Here the groups marked (1) and (2) may be assumed to change places, and as the form of the chain of carbonoids is such that it presents an entirely different aspect when viewed from the other side, the result of such a change of position would be to produce two isomers which would be related to one another, as an object and its mirrored image. It is possible that the two carbons may not be disturbed, the same effect being produced by the interchange of Hydroxyl and Hydrogen.

Many other examples of Isomerism of this type might be quoted, in which it is unnecessary to assume any spiral formation of the chain of carbonoids—the optical activity being due to a change in the position of the attached groups, without any alteration of the relative positions of the carbon atoms.

There remain, however, certain compounds of a different class in which there is considerable difficulty in ascribing the existing Isomerism entirely to a change in position of Hydrogen, Hydroxyl, or other groups in the molecule, and where it seems reasonable to suppose that the spiral form of the chain of carbons is involved.

We now turn to the consideration of some of the typical cases of compounds of this class containing four carbon atoms.

There are seven different arrangements of four carbonoids possible, as shewn in Figs. 46a and b, 47a and b, 48, 49 and 50, pp. 72a and b. If an additional carbonoid be added to one of the two groups of three carbonoids shewn in Figs. 44a and b, p. 72a, six new figures are produced, viz. : Nos. 46a and b, 47a and b, 49 and 50. In Fig. 46a and b the spiral chain is continued in the two mirror image forms, and in Fig. 47a and b two isomeric forms are produced of opposite configuration, but in Figs. 49 and 50 the enantiomorphous configuration disappears, and these Figures may be derived from either 44a or 44b, with the same result.

In the same way, the addition of a single carbonoid to either of Figs. 44a or 44b, if attached to either of the sides of the concave pair of faces of either a or b forms, will produce Fig. 49, in which again the spiral con-figuration has disappeared.

A single carbonoid can be added to Fig. 45, p. 72a in four ways : if it be attached to one of the end carbon-oids two figures are produced either 47a or 47b, which are mirror images of one another ; if attached to the middle carbonoid on either side Fig. 50 will be produced. Fig. 48 is produced by adding one carbonoid to the base of No. 45 on either side.

All the seven forms of four carbonoids can be pro-duced by different arrangements of Ethyloids except Fig. 50.

In the present state of our information regarding chemical transformations, there appears to be nothing to be gained by attempting to trace a correspondence between the changes of form effected by the addition of one carbonoid, as above stated, and the differences in form of compounds of three or four carbons. The compounds containing four carbons are mostly derived from the analysis of coal tar or from natural products, such as the acids of grapes and other fruits. The single carbon atom is not usually available, except in the saturated condition, and when changed to a nascent state by the loss of Hydrogen, it immediately forms a compound containing two or more carbons in the molecule.

But in whatever way the compounds of four carbons are formed, the carbonoid furnishes us with seven different configurations, some of which may have no counterparts in any compounds at present known, but others can fairly be assigned to well-known substances.

In order to limit the scope of this enquiry, we propose to consider certain typical cases of compounds containing four carbons only, viz :—

—A—   —B—

1. d— and l— Malic Acid   Crassulaic Malic Acid

$$\begin{array}{c}
\text{HO} \quad \text{H} \\
| \qquad | \\
\text{HOOC—C—C—COOH} \\
| \qquad | \\
\text{H} \quad \text{H}
\end{array}$$
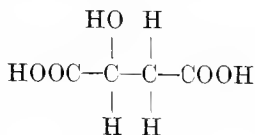
—A—   —B—

2. d—and —l Tartaric Acid   Mesotartaric Acid

$$\begin{array}{ccc} & OH & H \\ & | & | \\ HOOC— & C— & C—COOH \\ & | & | \\ & H & OH \end{array}$$
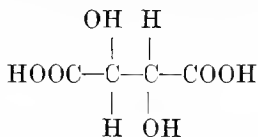
3.   Fumaric Acid   Maleic Acid

$$\begin{array}{ccc} & H & H \\ & | & | \\ HOOC— & C— & C—COOH \\ & | & | \end{array}$$
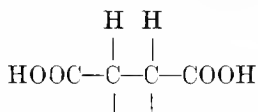
4.   Crotonic Acid   Isocrotonic Acid

$$\begin{array}{cccc} & H & H & H \\ & | & | & | \\ H— & C— & C— & C—COOH \\ & | & | & | \\ & H \end{array}$$
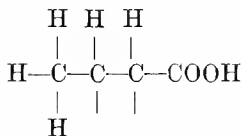
Each of the above four groups exhibits an Isomerism with well-marked differences between the Isomers, A and B, affecting both their chemical and physical characteristics, including melting point, etc., and in addition, Nos. 1 and 2 shew also another kind of Isomerism in which the two isomers, while agreeing in nearly all their characteristics, are distinguished by the power of deflecting the beam of polarised light—by one isomer to the right and by the other to the left.

Although there are difficulties to be met by any theory which seeks to explain this isomerism it is proposed to submit the suggestion that the carbon framework of all these compounds differs in its configuration,

e.g., dextro Malic Acid differs from lævo Malic Acid and these two again differ from Crassulaic Malic Acid, these differences being due to the arrangement of the carbon atoms within the molecule, which can be represented by differences in the arrangement of the four carbonoids.

The Carbon framework of the compounds appearing in Col. " B " above may be represented by one or more of Figs. 48, 49 or 50, pp. 72a and b, and the optically active isomers in Col. " A," Malic Acid and Tartaric Acid may be represented by the right- and left-handed forms shewn under Figs. 46a and b, or 47a and b. If this suggestion is accepted the opposite and equal optical activity of the two isomers will be satisfactorily explained, without having recourse to any assumptions with regard to the positions of the attached atoms of Hydroxyl and Hydrogen.

At the present time the peculiar Isomerism with which we have to deal, in the Malic and Tartaric Acids is attributed to the position in the molecule of the Hydroxyl or Hydrogen groups and to certain alleged changes in the directions along which the mutual attractions of the carbon atoms are supposed to operate.

Van't Hoff and Le Bel have also expounded the law that optical activity depends upon the presence in the molecule of an asymmetric carbon atom, and although some exceptions to this law have been discovered, it must be considered as holding good as a general rule.

The theory of Atomic Form attributes this right- and left-handed Isomerism to alterations in the form of the carbon framework, although it seems highly

probable that all such alterations are accompanied by changes in the positions occupied by the Hydroxyl and Hydrogen in attachment.

It has been assumed that the two isomers which represent the dextro and lævo modifications are distinguishable from one another by a difference in the arrangement of the attached atoms or groups, and that a further change in the positions of these groups is the cause of the additional Isomer such as Crassulaic Malic Acid and Meso-tartaric Acid. In Malic Acid, however, it is impossible to provide three different arrangements of the Hydroxyl group. In the formula

$$
\begin{array}{c}
\text{COOH} \\
| \\
\text{HO}-\text{C}-\text{H} \\
| \\
\text{H}-\text{C}-\text{H} \\
| \\
\text{COOH}
\end{array}
$$
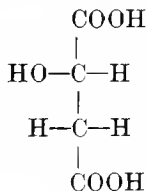
if it be allowed to rotate the molecule in the plane of the paper, and also around its longer axis, no effective variation can be made. If however only one change of position is allowed, viz., a rotation in the plane of the paper, two different formulæ can be designed, viz. :—

$$
\begin{array}{cc}
\begin{array}{c}
\text{COOH} \\
| \\
\text{HO}-\text{C}-\text{H} \\
| \\
\text{H}-\text{C}-\text{H} \\
| \\
\text{COOH}
\end{array}
&
\begin{array}{c}
\text{COOH} \\
| \\
\text{H}-\text{C}-\text{OH} \\
| \\
\text{H}-\text{C}-\text{H} \\
| \\
\text{COOH}
\end{array}
\end{array}
$$
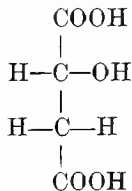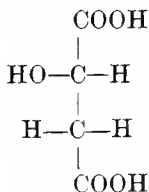
This leaves us without any further rearrangement possible—for Crassulaic Malic Acid—and even these formulæ are based upon the assumption of a difference in form between the back and front of the molecule, which is consistent with the view that the carbons have a definite geometric form, but which would not be appropriate, if the carbon is represented by a sphere —with equal attractions in four different directions in the plane of the paper—in which case, rotation around the longer axis would be possible. To meet this difficulty the following formulæ have been designed :—

I.	II.	III.
COOH	COOH	COOH
|	|	|
HO—C—H	HO—C—H	HO—C—H
|	|	|
HOOC—C—H	H—C—COOH	H—C—H
|	|	|
H	H	COOH
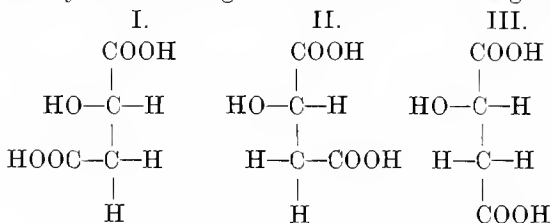
Formulæ I. and II. suggest that the Isomerism is due to a change in the position of the end carbons, and the formula is stated in such a way as to indicate a bend in the carbon chain to the right or left and in some measure accords with the theory of atomic form.

Stewart, in "Stereochemistry," after setting out the "physical and chemical differences between common Malic Acid and Crassulaic Malic Acid," writes as follows:—

"To account for this, it has been supposed that Malic Acid actually exists in three configurations (as shewn above), but this does not explain the effects which it produces upon the plane of polarisation. . . . . . The question of the Isomerism is undecided at present.

" Many other instances are known of isomerism for which our current views offer no explanation, and it seems advisable that further investigations in these fields should be carried out, in order that more facts may be accumulated."[1]

In explanation of the three formulæ on the preceding page, it is represented that they are projections of the Tetrahedral Models of Van't Hoff.—Malic Acid being represented thus :
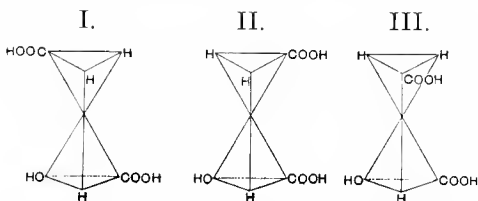
Here there are three possible arrangements, which are alleged to represent the two d— and l— modifications and Crassulaic Malic Acid.

The question arises what meaning is to be attached to these formulæ. Van't Hoff does not suggest that the atoms of Carbon have a tetrahedral configuration : he states that the molecule is a " stable system of *material points*,"[2] and he gives the extract from Pasteur's writings, quoted on p. 73. The carbon atom is represented as situated in the centre of a tetrahedron, from which its four affinities or bonds are directed to the four corners of the tetrahedron.

[1] Stewart, " *Stereochemistry*," 2nd Edition, (1919), p. 240.
[2] " *The Arrangement of Atoms in Space*," Van't Hoff, 2nd Edition, p. 5.

Later investigators generally have not materially varied these conceptions, and modern Text Books contain statements based upon similar conceptions of the carbon atom.

Cohen writes (1907)[1] :—

" The internal motion of the atoms may be   .   .   . disregarded, and the centres about which they oscillate considered as a statical system of material points.   How far the modern views of valency fit in with the idea of material points, whether the Valency of Carbon takes the form of a force acting in four directions, or of one evenly distributed over the atom ; whether it is determined by a tetrahedral figure of the carbon atom or depends upon the sub-division of the atom into smaller parts, it is not our intention to discuss."

Stewart, in *Stereochemistry* (1919),[2] says :—

" Many investigators have endeavoured to explain the origin of the tetrahedral grouping by assuming that the carbon atom is a material body of a certain shape and size.   It is not necessary to deal with these views here."

A large number of references are, however, given to the writings of foreign chemists.

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[1] Cohen's " *Organic Chemistry*," (1907), p. 67.
[2] Stewart's " *Stereochemistry*," 2nd Edition, p. 4.

Any student who attempts to form a mental image of the structure of the molecule of Malic Acid is confronted with a difficult task,—he must imagine the carbon atom a system of *material points*, assumed to be held in its place in the molecule by forces acting through the points of a hypothetical tetrahedron, but which nevertheless must not be considered as being a body of any definite shape.

The back-bone of the molecule of Malic Acid is clearly the chain of four carbon atoms, which appears in the Tartaric, Succinic and Crotonic Acids and in Fumaric and Maleic Acid, but these atoms are supposed to be united in the middle of the chain in such a way that rotation of the two upper carbons takes place around an axis passing through the *points* of two tetrahedra ; no consideration being given to the method of union between the two carbon atoms forming the upper and lower halves of the molecule.

In the place of these conceptions, the Theory of Atomic Form places before us a carbon atom of a certain shape, which naturally and inevitably combines to form two kinds of carbon chains, related to each other as object and image, the optical isomerism being considered as due to the configuration of the carbon chain, with or without any modification in the positions of the attached atoms or groups.

It may be acknowledged that the tetrahedral conception which we owe to Van't Hoff and Le Bel has helped forward the study of optical Isomerides, but it is also true that a step forward is needed to enable clear and definite conceptions to prevail.

We are therefore unable to accept the above three formulæ (p. 85) as a correct representation of the arrangement of the atoms in the two optical Isomers of Malic Acid, and in Crassulaic Malic Acid, which differs so markedly from them both.

With regard to the dextro and lævo forms of Tartaric Acid and Meso-tartaric Acid, the usual formulæ are as follows :—

I.	II.	III.
Dextro	Lævo	Meso
COOH	COOH	COOH
|	|	|
H—C—OH	HO—C—H	HO—C—H
|	|	|
HO—C—H	H—C—OH	HO—C—H
|	|	|
COOH	COOH	COOH
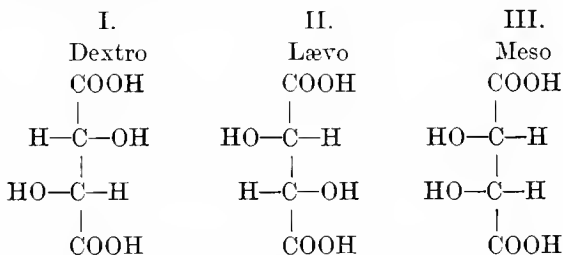
These formulæ are open to the objection already stated in connection with Malic Acid.

There are considerable differences both chemical and physical between the ordinary Tartaric Acids and the Meso-tartaric type, while the differences between the dextro and lævo forms of the Acid are limited to the effect produced upon the ray of polarised light and the form of their crystals. It is submitted that, with such material differences as are shewn to exist between the ordinary Tartaric Acid and the Meso type, it is inconsistent to assign to the latter such a slight change in the arrangement of the constituent atoms as is shewn by the formula stated above ; or if the large difference between the optically active and the Meso

Form is properly represented by the change in the position of one of the Hydroxyl groups—it is then inconsistent that the comparatively slight difference of character between the dextro and lævo modifications should also be represented by a similar change in the position of both Hydroxyl groups as shewn in the formula. The isomerism of the dextro and lævo forms of Tartaric Acid is entirely different in character from that of Meso-tartaric Acid and calls for a well marked difference in the structure of the Meso as compared with the Racemic type.

These difficulties are entirely removed if the modifications in the carbon chain shewn in Figs. 46a and b, 47a and b and Figs. 48, 49 and 50, pp. 72a and b are adopted.

On the other hand, it is at first sight somewhat difficult to assume that these modifications of the carbon chain can be made with the comparative ease which appears to be indicated in some of the reported reactions.

By the Walden Inversion—*lævo*-Malic Acid can be converted, by the action of PCl_5 into *dextro*-Chloro-Succinic Acid, and this again by the action of AgOH into *dextro*-Malic Acid, thus effecting the change from the *lævo* form of Malic Acid into the *dextro* form—and this change is reversible. If the theory of Atomic Form be adopted, this involves a change in the arrangement of the carbon framework from Fig. 46a to 46b. This does not seem so unlikely when the magnitude of the molecules taking part in the reaction is borne in mind —$PCl_5 = 208$, $AgOH = 125$. It seems fair to assume that the addition of a chlorine atom and its subsequent removal may be responsible for a rearrangement

G

of the carbon atoms in the molecule, the amount of change in the carbon framework of the molecule being comparatively slight as we shall shew presently.

A greater difficulty arises however when we consider the statement that Malic Acid is lævo-rotatory in dilute solutions but becomes dextro-rotatory when the concentration is increased[1] Stewart adds :

> " In this case no change of configuration can be assumed ; and it is evident that configuration and sign of rotation do not necessarily go hand in hand."

Cohen,[2] commenting on this peculiarity of Malic Acid, says :

> " The change of sign in the rotation of Malic and Tartaric Acids . . . . . has been attributed to the presence of molecular aggregates in the concentrated solution of opposite rotation, just as crystal aggregates of a compound have been found which differ in sign from their solutions. Imperfect electrolytes, like the organic acids, exhibit in solution a series of changes which depend generally on the degree of dissociation.

> " The extent of dissociation is increased by dilution and by rise of temperature, with a corresponding numerical change in rotation."

It is scarcely possible on the strength of these instances alone, to give up the view so long held, that a change in optical rotation is associated with some rearrangement of the atoms comprised in the molecule.

---

[1] Stewart—" *Stereochemistry*," 2nd Edition, (1919), p. 69.
[2] Cohen—" *Organic Chemistry*," 2nd Edition, Part II. Structure, p. 231.

This view is strongly supported by the facts regarding the separate crystallisation of the dextro and lævo modifications and the right- and left-handed forms of the crystals.

The existence of this enantiomorphous configuration of the crystal, points to a difference in the method of arrangement of the molecules in the crystal, which is believed to be associated with a difference in the configuration of these molecules.   If the molecular forms are identical and the change of sign of rotation is independent of configuration, it is difficult to see how two equal and opposite forms of the crystal can be obtained.

If it be conceded that the molecule of an optically active isomer has a configuration which is the mirror image of the other isomer into which the compound is divisible, the question arises whether this form is due to the arrangement of attached groups, such as Hydroxyl or to an enantiomorphous configuration of the carbon framework of the molecule or to both causes together.

A study of the models shewn in Fig. 46, p. 72b, shews that the two forms are so exactly alike in all respects, except that one has a right-handed and the other a left-handed configuration, and they appear to lend themselves so easily to the building up of two equal and opposite crystalline forms, that it is difficult to reject the view that in these models we have an explanation of the phenomenon of optical activity.

The law of Van't Hoff and Le Bel and the persistency with which the presence of an asymmetric carbon atom in the molecule is associated with optical activity is partly explained by the following considerations.

In the cases of carbon chains of 3, 4 and 5 carbons, nearly all the active compounds possess an Hydroxyl group, or some other atom or group of considerable size, the presence of which on one side of the chain and of a Hydrogen atom on the other side appears to be associated with optical activity, such an arrangement of the attached atoms and groups may probably be associated with the spiral character of the chain of carbonoids; it naturally leads to the existence of an asymmetric carbon atom.

As soon, however, as the Hydroxyl is removed, the optical activity disappears. This is the case with Succinic Acid, Fumaric and Maleic Acids and the Crotonic Acids. Succinic Acid is saturated with Hydrogen, but in the other Acids there is the difference between a Hydrogen linkage on one hand and an unsaturated condition on the other—a difference which might be expected to lead to optical activity in the Isomers, but none has been observed.

It should be noted that in these optical Isomers, there are two conditions to be fulfilled in order that optical activity may be evident :

(1) The compound must exist in two optical Isomers.

(2) Means must exist whereby a separation of the two optical Isomers can be made.

It is suggested that the presence of the Hydroxyl or other large group in the molecule renders the separation of the two Isomers possible, no separation taking place when the only difference is in the form of the carbon chain or a difference in arrangement of the attached Hydrogen.

So long as no separation has been effected either during natural development or by artificial means, no optical activity can be discovered.

CHANGES IN THE CARBON FRAMEWORK.

It is clear that the form of the carbon framework must be subject to change in some circumstances, for instance, the following changes are recorded :—

1. Malic Acid on heating produces both Fumaric and Maleic Acids, the particular Acid produced depending upon the temperature employed and the method of heating.[1]

2. On oxidation, Fumaric Acid produces Tartaric Acid and Maleic Acid produces Mesotartaric Acid.[2]

3. When acid is added to Sodium Thiosulphate in presence of Maleic Acid, Fumaric Acid is produced.[3]

4. When Bromine acts upon Maleic Acid, Isodibromo-succinic Acid is formed.[4]

5. When Bromine acts upon Fumaric Acid, Dibromo-succinic Acid (meso form) is produced.

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[1] Holleman—" *Text Book of Organic Chemistry*," Fifth Edition, p. 211.
[2] Holleman—" *Text Book of Organic Chemistry*," Fifth Edition, p. 244.
[3] Stewart—" *Stereochemistry*," 2nd Edition, p. 122.
[4] Stewart—" *Stereochemistry*," 2nd Edition, p. 116.

6. Both Fumaric and Maleic Acids yield Succinic
    Acid on treatment with Sodium Amalgam and
    Water, and both Acids may be transformed
    into Malic Acid by heating with water at a
    high temperature.[1]

The differences in character of Fumaric and Maleic
Acids indicate that one of them (probably Maleic Acid)
has the indivisible form Figs. 48, 49 or 50, pp. 72a and b,
and that Fumaric Acid has the same configuration as or-
dinary Malic Acid and ordinary Tartaric Acid. If this be
so, the oxidation of Fumaric and Maleic Acids and the
production of the two forms of Tartaric Acid would be
accounted for. Fumaric Acid however has never been
divided into dextro and lævo forms. A similar absence
of optical activity is observed in ordinary Crotonic
Acid and Succinic Acid.

The models which at first sight appear most suitable
to represent Fumaric and Maleic Acids are Nos. 48 and
49, which have somewhat similar forms and can easily
be converted and re-converted from one form to the
other. It would be satisfactory if we could assign the
two faces occupying the opposite sides of the concavity
to the two unoccupied faces of the molecule, but if this
is done the formulæ of these acids would have to be
altered to

$$O \quad\quad H \;\; H \quad\quad O$$
$$\diagdown \quad\quad | \;\; | \quad\quad \diagup$$
$$-C-C-C-C-$$
$$\diagup \quad\quad | \;\; | \quad\quad \diagdown$$
$$O \quad\quad H \;\; H \quad\quad O$$
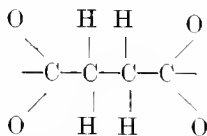
[1] Holleman—" *Text Book of Organic Chemistry*," Fifth
Edition, p. 212.

and there would be difficulty in arranging for the acid radicle COOH.   It is not improbable that the two opposing sides of the concavity are occupied by the acid radicle and that the unsaturated faces are to be found on the two middle carbonoids.

On treatment with sodium amalgam and water, both acids would be broken in the middle at the position of the so-called double bond, and when reunited might produce a new form, say Fig. 48, which would easily take up two atoms of Hydrogen with production of Succinic Acid.

No decision as to the models of Fumaric and Maleic Acids can however be made at present.

Of the Reactions enumerated above, Nos. 3, 4 and 5 seem to indicate that the arrangement of the carbon framework of these acids can easily be changed from one form to another.   We shall now proceed to consider the extent of these intra-molecular changes.

It has already been pointed out, p. 79, that the addition of one carbonoid to the two tri-carbonoids which are associated as object and image, Fig. 44a and b, p. 72a, may produce six different forms of tetracarbonoids, and that in some cases the group loses altogether its optical activity and produces one of the forms of carbonoid aggregates which is not associated with optical isomerism.

Similar effects can be produced by changes in the positions of the carbonoids in the groups of Tetra-carbonoids shewn on p. 72b.   Fig. 46 (a) can readily be changed into 46 (b), Fig. 51, p. 96, is a diagramatic representation of 46 (a) consisting

of two Ethyloids, united at the dotted line a—b, which represents a possible line of fracture. If then the molecule be broken along this line and the two Ethyloids are turned as if the line a—b were a hinge, then the face (c) would approach face (d) until a reunion of the two Ethyloid groups would take place by the attachment of (c) to (d).

By this means a similar molecule would be produced, but it will have the reverse configuration, see Fig. 52.
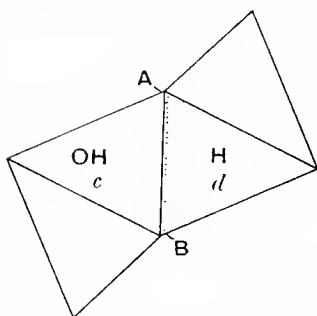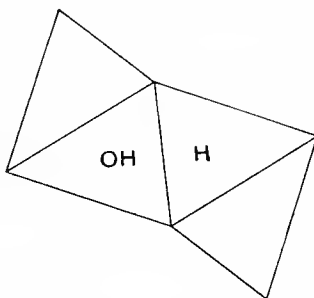
Fig. 51   Fig. 52

Some alteration in the position of the attached Hydrogen and Hydroxyl will be necessary, but this should not be difficult, if the forces at work on this molecule are sufficient to break the carbon chain along the line A—B.

The position of the two acid groups COOH will remain unaltered.

This change corresponds to what may be expected to take place when Dextro Malic Acid is converted into the lævo modification.

A diagram of the model 46a is shewn below. See Fig. 53. If the end carbonoid marked x shifts its position to the face y by revolving around the point * so that b is at the point C and A at the point b, an entirely new figure, No. 54, is produced, which unlike Fig. 46, is free from enantiomorphism, and both 46a and 46b can thus be readily changed into Fig. 54.
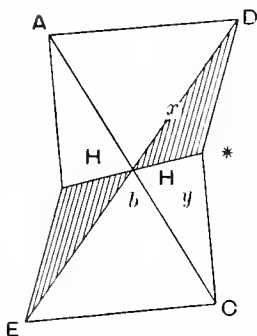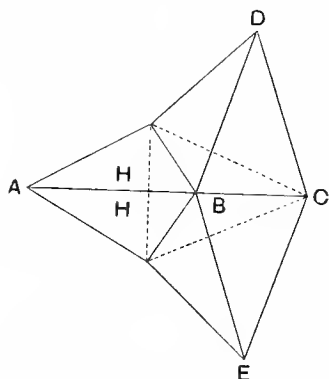
Fig. 53   Fig. 54
(See also Fig. 50, p. 72a)

The only change in the attached atoms is the removal of Hydrogen from the face y to a similar position on that face of the adjoining carbonoid previously occupied by the carbonoid x.

The solid angle which separates this face from the face y is very obtuse, and the sliding of the carbonoid from one position to the other can very easily take place.

This change corresponds to what may be supposed to take place when the ordinary forms of Malic Acid dextro and lævo are both changed into Fumaric or Maleic Acid.

Many other similar transformations can take place by the change of linking of the carbonoids or Ethyloids with comparatively slight changes of position in the carbonoid aggregate. These can best be discerned with the help of a model, when the changes can be traced and the results seen, but sufficient has been shewn to illustrate the readiness with which the form of the molecule may be changed and the enantiomorphism lost or regained.

Sufficient has perhaps been stated to justify the view that the new theory ought not to be put aside on the ground of the changes of form required in the carbonoid aggregate.

It may fairly be argued however that the well-known stability of the carbon chain renders it unlikely that a change of structure will actually take place, such as has been proposed. In this connection it is pointed out that in certain circumstances a carbon chain may be broken and the molecule decomposed—as an instance take Trimethyl Carbinol :

$$H_3C$$
$$H_3C—C. \ OH$$
$$H_3C$$
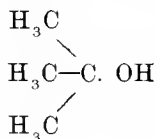
the Carbon framework of this substance being represented in Fig. 50, p. 72a, which on oxidation breaks up

into substances with a smaller number of carbon atoms. Oxidation of tertiary alcohols generally results in a breaking up of the molecule.

Another case of intramolecular transformation will be found in the formation of Pinacoline

$$(CH_3)_3 . \; C. \; CO. \; CH_3$$
$$(x) \; (y)$$

$$OH$$
from Pinacone $(CH_3)_2 \; C(OH)\!-\!\overset{/}{\underset{(y)\diagdown}{C}}\!-\!CH_3$
$$(x) \qquad\qquad CH_3$$
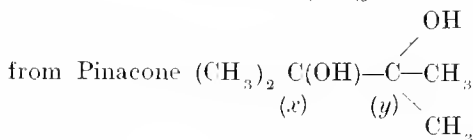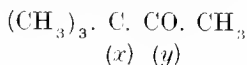
here the methyl group is moved from C in Pinacone to C in Pinacoline. (y) (x)

According to the models (and assuming that the position of the carbonoids is accurately represented by the formulæ) this change is due to a movement of a carbonoid, which involves considerable alteration in its position in the molecule and results in a different configuration of the carbon framework.

With regard to molecules containing five or more carbon atoms, it must be pointed out that among the amyl alcohols there are two—secondary Butyl carbinol and Methyl Propyl Alcohol—which are active compounds.

Of the other amyl alcohols there are four in which the carbon frame-work is such that no enantiomorphous configuration is likely, viz. :—

> Isobutyl carbinol.
> Methyl isopropyl carbinol.
> Dimethyl ethyl carbinol.
> Tertiary butyl carbinol.

Diethyl Carbinol appears to have a form which is inactive, although other forms can be designed which would produce active isomers, but the latter appear to be probably unstable.

There remains the normal primary Amyl Alcohol, which appears to consist of a normal chain of Carbon with the Hydroxyl attached to the end carbon.

A simple chain of five carbonoids will have the spiral formation and should exist in two active isomers. The fact that the Hydroxyl group is attached to the end carbon

$$
\begin{array}{ccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
| & | & | & | & | \\
\text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{OH} \\
| & | & | & | & | \\
\text{H} & \text{H} & \text{H} & \text{H} & \text{H}
\end{array}
$$

may render the two isomers inseparable; it seems doubtful if any means at present exists for removing the Hydroxyl from one of the two isomers in preference to the other.

With regard to substances containing six or more carbon atoms, arranged in a normal chain, such molecules should exhibit the spiral structure, and therefore should give rise to optical isomerism.

Compounds of six or seven carbons may exist in which the position of branched chains may prevent the formation of a spiral chain, such as for instance :—

$$
\begin{array}{ccc}
\text{C} & & \text{C} \\
\diagdown & & \diagup \\
& \text{C} - \text{C} - \text{C} & \\
\diagup & & \diagdown \\
\text{C} & & \text{C}
\end{array}
$$

In this case, if the compound is balanced so that the attached atoms or groups on either hand are equal, no optical activity will arise, but in the case of a normal chain C—C—C—C—C—C—C—the carbonoids will be arranged in a spiral form.

It may be asked what form are we to assign to the normal chains in the well-known Homologous series, the Paraffins, Olefines, Alcohols and Ethers.

With regard to the Paraffins, the normal chains of three or more carbons should be arranged in a spiral formation, and the compound should exist in three isomeric forms, d, l, and racemic. Is this the case ?

According to Holleman, optical activity exists in the Petroleums[1] when in the natural state. The particular substance which gives this character to the mixture of Hydrocarbons which make up Petroleum does not appear to have been isolated, and the optical activity may be due to some impurity. If, on the other hand, it is established that some of the Paraffins and Olefines exist in two active isomers, the above question will be satisfactorily answered.

Some of the higher Alcohols may be expected to shew optical activity, but the peculiar configuration of the Ethers does not seem to lend itself to this form of Isomerism.

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[1] Holleman—" *Text Book of Organic Chemistry*," Fifth Edition, p. 40.

CHAPTER X.

CONDENSED RINGS.

The consideration of those compounds which according to the usual formulæ comprise two or more condensed Rings is a matter of special importance, because it is impossible to prepare combinations of Benzenoids which will represent these formulæ. Two Benzenoids in the same plane cannot be united by having two carbonoids common to the two rings.

At the outset this fact appeared to present a difficulty in the way of the acceptance of the theory of Atomic Form.

With regard to Naphthalene $C_{10}H_8$, the following is the usual formula.
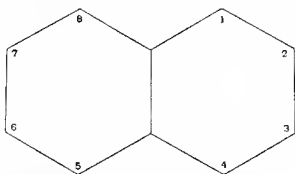
The consideration of the oxidation of α Nitronaphthalene and of α Naphthylamine and the oxidation of Quinoline to Quinolinic Acid on the one hand, and to a derivative of Anthranilic Acid on the other, appeared to justify the acceptance of the recognised formula for Naphthalene.

Moreover, the fact that Isoquinoline on oxidation yields a mixture of Phthalic Acid and Cinchomeronic Acid seems conclusive on this point.
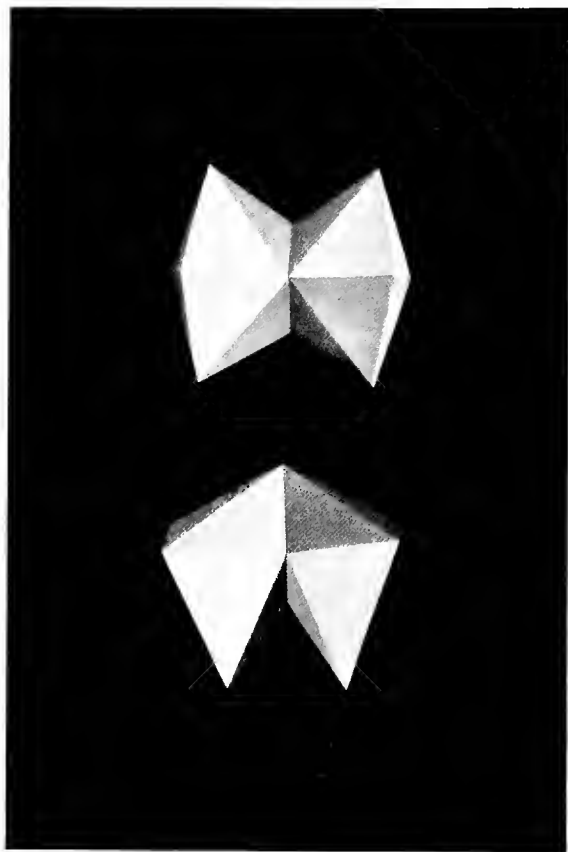
Fig. 55
NAPHTHALENE

Fig. 58
*O.*XYLYLENE, showing Di-ethyloid Group

| Cinchomeronic Acid. | Isoquinoline. | Phthalic Acid. |
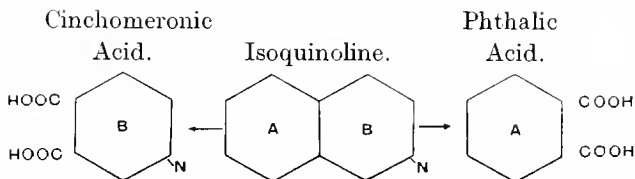
The formula for Isoquinoline is C_9H_7N, and the Nitrogen atom forms part of the Ring B which persists in the formula for Cinchomeronic Acid, while Ring A, in which there is no Nitrogen, gives rise to Phthalic Acid.

Further consideration of the models shews however that an arrangement of 10 carbonoids can readily be made, in which two groups of four carbonoids each are united by an ethyloid as in photograph shewn in Fig. 55, p. 103a.

It is suggested that this photograph gives a faithful representation of the formula of Naphthalene, which may be represented thus :—

$$C_{10}H_8$$
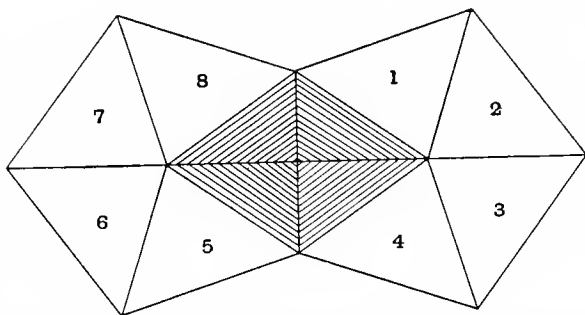
Fig. 56

NOTE.—This diagram shews the central Ethyloid group, which in fact is covered by the two di-ethyloids.

Naphthalene would thus appear to have the same configuration as the tetracarbonoid shewn in Fig. 49, p. 72b, and which will in future be described as a di-ethyloid.

Naphthalene may be compounded of five ethyloids arranged so as to produce one molecule of the form shewn above. As explained under Cyclo-pentane, chapt. XI. the group of two ethyloids or four carbonoids shewn in Fig. 49, leaves a gap between the two end carbonoids approximately equal to another carbonoid. It is this gap that is filled by one of the carbonoids of the central ethyloid group, the other carbonoid of the ethyloid carrying another Di-ethyloid group similar to the one first mentioned and depicted in Fig. 49.

The gap in the Di-ethyloid Ring fits almost exactly to the carbonoid and will certainly make a stable arrangement almost equal in stability to a Benzene Ring.

The eight Hydrogen atoms fall naturally into their places 1 to 8 as marked in the above formula, and there is no opportunity for attaching any other Hydrogen atoms except on the other side of the molecule, which, as in Benzene, is unsaturated.

This formula is also applicable to isoquinoline and accords with the results of oxidation as shown above. When the isoquinoline molecule is broken up one di-ethyloid is removed and the other di-ethyloid plus the ethyloid which is common to the two rings will form a Benzene or pyridine Ring without changing the positions of the attached Hydrogen ; but a general rearrangement of the carbonoids is necessary. The

changes necessary to effect this and the positions in the molecule retained by the attached Hydrogen are difficult to describe, but can readily be appreciated with the help of the models.

The monosubstitution products of Naphthalene are divided into two series, α and β, the former being cases where the substitution takes place on a carbon atom directly linked to the adjacent Ring, 1, 4, 5 or 8, and the β series representing those in which substitution takes place at 2, 3, 6 or 7, see formula, on page 103.

The formula for Napthalene, Fig. 56, p. 103, shews that the occupied faces are divisible into two series according to the position of the carbonoids, Nos. 1, 4, 5, 8, being situated close together in the centre of the molecule, and No. 2, 3, 6, 7 occupying positions further removed from the centre.

The synthesis of Naphthalene from Benzene Vapour by passing it through a *white* hot tube is quite consistent with the configuration shewn above.

It is clear that the rise of temperature involved in this synthesis is sufficient to break up the Benzene Ring into three Ethyloids, many of which will recombine in a different way so as to produce the molecule of Naphthalene. We have already noticed the great stability of the Ethyloid, and it is improbable that the rise of temperature in a *white* hot tube will be sufficient to break up the Ethyloids into single carbonoids ; if, however, this breaking up should take place, the Ethyloids would be re-formed as soon as the temperature is lowered.

H

Another synthesis of Naphthalene is from *o-Xylylene* Bromide.

$$CH_2Br$$
$$/$$
$$C_6H_4$$
$$\backslash$$
$$CH_2Br$$
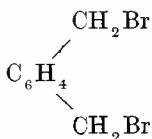
This compound, when freed from the two Bromine atoms, presents the curious feature that the two CH_2 groups in combination with two of the carbons of the Benzene Ring form a group of four carbons and in representing this group by our models, we find that it is arranged relatively in the same way as the Di-ethyloid Group, see the photograph, Fig. 58, p. 103a.

o-Xylylene may therefore be represented by the following formula.

Di-ethyloid
Group
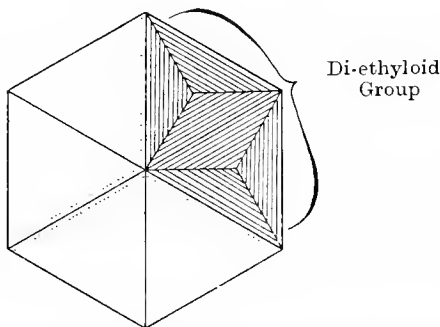
Fig. 57
The dotted lines represent the probable lines of fracture

The reactions which subsequently take place during the synthesis of Naphthalene involve the use of the very large molecule of tetra-disodio-ethane-tetra-carboxylate and appear to be sufficient to disturb the stability of the Benzene Ring causing a rearrangement in the form required to produce the configuration shewn in Fig. 55, p. 103a.

It is also noticeable that it is only the *ortho* compound which is capable of producing the di-ethyloid group. In the meta and para compounds no such group will arise; this feature also corresponds with the fact that it is only the *ortho* xylylene that can be used to synthesize Naphthalene.

Another synthesis of Naphthol, a derivative of Naphthalene, is from Phenyl Vinyl Acetic Acid. There are five acids isomeric with Vinyl Acetic Acid of the formula $C_4H_6O_2$, but there are only four formulæ available for representing them. It seems probable that one or more of these acids differ from the other isomers in the arrangement of the carbon framework, and may have the form of the di-ethyloid. If this be the case the formation of Naphthalene from this compound is a confirmation of the suggested configuration.

The oxidation of Naphthalene to Phthalic Acid seems to point to the existence of a Benzene nucleus as part of the molecule ; this however is not certain.

The following quotation from Cohen's *Text Book of Organic Chemistry* points to the possibility of a constitution for Naphthalene in which the constituents, although not forming a Benzene Ring, are readily convertible into such a group :—

[1]" Does the formation of Benzene derivatives from Naphthalene, and both Benzene and Pyridine derivatives from quinoline and isoquinoline, necessarily imply the pre-existence of these nuclei in the original compound ?

" Although at first sight an affirmative reply to the question appears the most simple and obvious one, Bamberger has shewn that there are many experimental facts which are opposed to it, and he prefers to regard all three compounds as represented by a ring of 10 atoms, in which the 4th Carbon or 3rd Nitrogen bonds as the case may be, are directed towards the centre of each nucleus."

The Theory of Atomic Form does not make it necessary to account for all the unoccupied faces of the molecule, and allows for some of these to remain unsaturated both in the Benzene Ring and in Naphthalene, the position of the molecules in space and their rotational movements being considered to be sufficient to account for the unsaturated condition of the molecule.

---

[1] Cohen—" *Organic Chemistry*," 2nd Edition, Part III., p. 283.

ANTHRACENE AND PHENANTHRENE $C_{14}H_{10}$.

The recognised formulæ for these two compounds are:

Anthracene
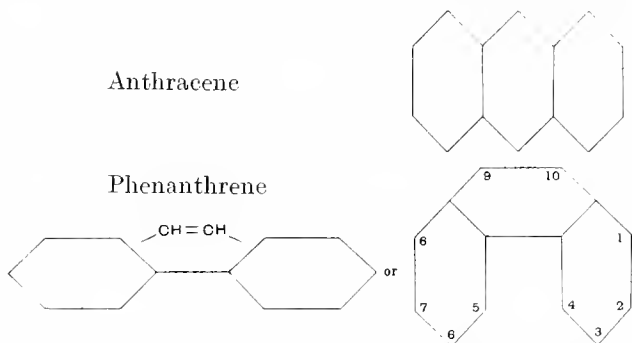
Phenanthrene

Except as regards the first formula for Phenanthrene there is a difficulty in representing these formulæ by the models of the Benzene Ring, as they involve the *condensed* Ring system.

As regards Anthracene, a simple formula of two benzenoids linked together by two carbonoids supplies a model of this compound, in which, however, there is no hydrogen attached to the two central carbonoids which form the link between the two Benzenoid Rings. See the following formula:
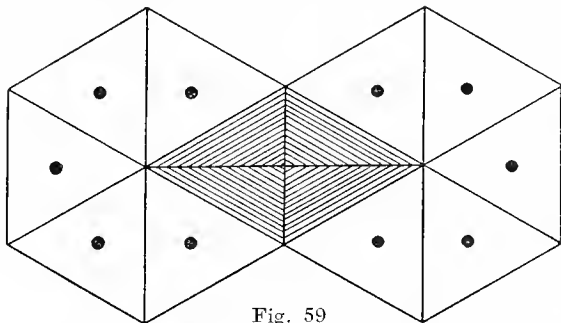
Fig. 59
The spots represent attached hydrogen.

The synthesis of anthracene from benzene and tetra-bromo-ethane is consistent with this model. On removal of Bromine from the tetra-bromo-ethane there remains a single Ethyloid which without change can form the link between two Benzene rings, but which would have to be broken up into single carbons in order to link together these two rings in *two* places.

The Hydrogen attached to this Ethyloid appears to be removed by the Bromine; this may quite probably be the case, leaving five atoms of Hydrogen in attachment to each of the two Benzene rings. This arrangement of the Hydrogen is at least quite as probable as that proposed in the condensed ring formula.

The production of Anthraquinone by oxidation of Anthracene will result by the attachment of two oxygen atoms to the two Benzene rings, reducing the number of Hydrogen to 8.

The point of difficulty is whether the link consists of two carbons in the ortho position or not; the synthesis of Anthraquinone from Phthalic Anhydride and Benzene may be considered as furnishing proof of the existence of two carbons in the ortho position, but the evidence does not appear to be conclusive on this point.

PHENANTHRENE.

The existence of a condensed ring in the constitution of Phenanthrene is certainly a matter of doubt.

In Stilbene $\quad\quad$ CH—C$_6$H$_5$

$\quad\quad\quad$ (a) ||

$\quad\quad\quad\quad$ CH—C$_6$H$_5$

the two carbons which connect the two phenyl groups
are not linked to them in *two* positions having regard
to the number of Hydrogen atoms attached to these
groups. The red hot tube enables the compound to
throw off two Hydrogen atoms, which may be with-
drawn from the link C$_2$H$_2$ or from the rings, reducing
them to C$_6$H$_4$, but there is no evidence that the C$_2$H$_2$
is linked to two places in each of the rings, and the
facts with regard to the addition of Bromine and
Oxygen to the link seem to negative the view that there
is a third ring in Phenanthrene.

It is suggested that this compound may be a
diphenyl with two carbons attached, in which case the new
formula for Phenanthrene would be expressed thus :—

Fig. 60

CH—C$_6$H$_4$—C$_6$H$_4$—CH

When Stilbene Vapor is passed through the red
hot tube it is suggested that a fracture takes place at
the point (a) and that the two phenyl groups after
losing two Hydrogen atoms, unite to form a group of a
diphenylic character.

$$\begin{array}{ccc} \text{CH} & & \text{CH} \\ | & & | \\ C_6H_4 & \!\!\!\!-\!\!\!\!- & C_6H_4 \end{array}$$
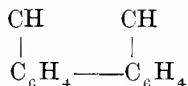
There is no attachment between the two carbonoids
at (β) which meet at their edges and the molecule would
be likely not to be very stable.   It melts at 96°, Anthra-
cene 213°, and dissolves in Alcohol more readily than
Anthracene.

We do not consider however that in this case the
carbonoid model accords in all respects with the mole-
cule of Phenanthrene, and we think that the form of
the model must be reserved for further consideration.

Other models can be prepared representing in
different forms the complete series, from Naphthalene
$C_{10}H_8$ to Chrysene $C_{18}H_{12}$, but they do not accord
with the accepted formulæ, and there are some points
of difficulty in connection with them which cannot at
present be explained.   It therefore appears to be best
to await further knowledge in connection with the
subject of this chapter.

CHAPTER XI.

CYCLIC COMPOUNDS.

The Heterocyclic compounds, containing other elements such as Nitrogen, Oxygen, Sulphur, etc., are considered to be outside the scope of this work, which is confined to carbon compounds.

The substances with which we propose to deal are therefore :—

> Cyclo-Propane
> Cyclo-Butane
> Cyclo-Pentane
> Cyclo-Hexane

also the higher cyclic compounds, Cyclo-Heptane and Cyclo-Octane.

Cyclo-Hexane. This is a Benzene derivative, represented so far as the carbon framework is concerned by the Benzenoid which has already been discussed in Chapter III.

It is produced by mixing Benzene vapor with Hydrogen over finely divided Nickel at a temperature of over 150°, also by the action of Palladium black on Benzene and Hydrogen; by this means combination of Benzene and Hydrogen takes place—the compound clearly contains a six membered ring, and its configuration is well-known.

Phloroglucinol and Hexahydroxy Benzene may also be considered as being Benzene derivatives and having the Benzenoid configuration.

In the cases of some other derivatives containing six carbons, the cyclic form is not so clearly indicated, and it seems possible that some of these compounds may be unsaturated—it is unnecessary, however, to decide this point, as our models provide for cyclic formation in the case of all compounds containing five or six carbon atoms.

CYCLO-PROPANE. With regard to cyclo-propane and cyclo-butane, the carbonoid aggregates are unable to form closed rings of 3 or 4 carbonoids only.

If we adopt the theory that as the carbon chain is lengthened it tends to bend round, so that its ends approach each other, until the compound containing five atoms is reached, the configuration of the cyclic compounds of 3, 4 or 5 carbons can be illustrated by the following scheme :—
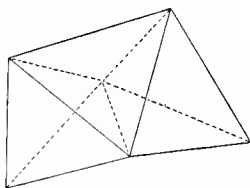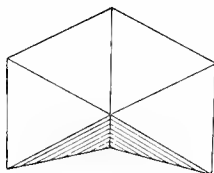
Fig. 61   Fig. 62
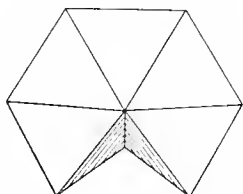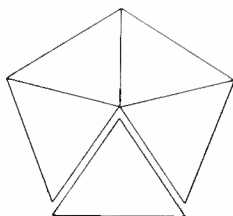
Fig. 63a   Fig. 63b

But these figures do not represent true cyclic configurations except in the case of the second form for Penta-carbonoid, Fig. 63b. In this form we have a figure which is in reality a closed ring. It has already been referred to in Chapter X. in connection with Condensed Rings. Although the fifth carbon atom does not fill the space in the Ring with the exactitude of the carbon atoms in Benzene, yet it is almost a precise fit, and one which clearly prevents the existence of any unoccupied faces and must render the molecule stable.

In Fig. 63a, there is more opportunity for instability in the structure, but the two opposing faces at the ends of the chain are in such a position that they will probably remain unoccupied by any atom larger than hydrogen.

The stability of cyclo-pentane and its derivatives is well-known; it does not yield any addition product with Bromine, and is as stable towards Nitric and Sulphuric Acids as a saturated Hydrocarbon. It also resists boiling with Hydriodic Acid, and is the most stable

of the cyclo-paraffins. From the results now available it may be said that in compounds of five or six carbons, we may have rings of much greater stability than those where there are a greater or less number of carbon atoms in the molecule.

Our models shew that it is only the aggregates of five or six carbonoids which are capable of true ring formation, and that of the two forms the Benzenoid is the most stable, while the model of cyclo-pentane, Fig. 63b, approaches it in stability very nearly.

Let us now consider the evidence in favour of ring formation in the cases of cyclo-propane and cyclo-butane.

The synthesis of the former is as follows :—

Allyl Alcohol $CH_2—CH—CH_2OH$

—OH   + Br

   $= CH_2—CH—CH_2Br$

+ H Br $CH_2Br—CH_2—CH_2Br$
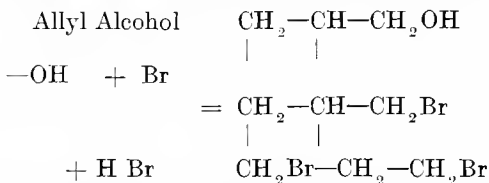
by the action of sodium 2Br, are removed, leaving

cyclo-propane $CH_2—CH_2—CH_2$

this substance is not identical with propylene—

   $CH_2—CH—CH$
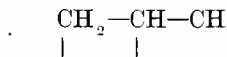
It has been assumed that the formula of cyclo-propane should be written thus :

$$CH_2$$
$$CH_2$$
$$CH_2$$
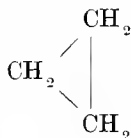
but if this synthesis is critically examined in the light of the theory of Atomic Form, there will be found nothing to support the view that the above " ring " formula is correct.

Those who adopt the theory of Atomic Form will also adopt the view that in carbon chains faces may be unsaturated, but such unsaturated faces will be always in *pairs*, either on adjoining carbonoids or on the faces occupying corresponding positions at the two ends of the carbon chain ; the existence of these pairs being due to the configuration of the carbon chain as explained in Chapter V. under the head of " Law of Even Numbers."

It has been already stated that the idea of a double bond must be rejected, and a pair of unsaturated faces substituted ; the existence of unsaturation in these cases being justified by the consideration of the position of the faces in the chain and the probable axis of rotation of the molecule ; moreover the readiness with which addition products are produced amounts almost to proof of the unsaturated character of these pairs of faces.

In the case of cyclic compounds—cyclo-propane and cyclo-butane—it has been impossible to adopt the idea of a double bond, and it is submitted that in these cases chemists have had recourse to the idea of cyclic formation in order to satisfy the current theories in regard to saturation and having regard to the differences in Chemical and Physical Characteristics between the cyclic compounds and the isomeric Olefines.

If we adopt the theory of Atomic Form, we assume that these unsaturated faces are available for the formation of addition products. Cyclo-propane is acted upon

by Hydrochloric, Hydrobromic, and Hydriodic Acids
and also by Sulphuric Acid, but it does not appear to
be acted upon as easily as its isomeric Olefine, for
instance, it is not attacked by Permanganate, and
Bromine acts upon it slowly.

It will be seen on referring to Fig. 44a and b and 45,
p. 72a, that either of these figures may be chosen to repre-
sent cyclo-propane. If we adopt Fig. 44a and b, we shall
have to consider this substance as being a mixture of
the right and left-handed forms ; this is possible, but
the two active isomers have not so far been separated.
If we adopt Fig. 45, we must not assume that the two
co-planar faces at the base of the figure are unsaturated,
as if this were the case, two molecules would immediately
join to form a Benzene derivative—cyclo-hexane.

There seems no reason why we should assume that
the two co-planar faces are unsaturated. The position of
the Hydrogen may be as shewn in the following diagram :
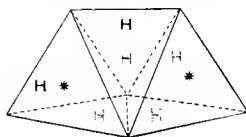
Fig. 64

In the two isomeric forms, Fig. 44a and b, we may
assume that it is the two faces on the opposite sides
of the concavity that are unsaturated ; this would
accord better with the features of cyclo-propane, as
there might be more difficulty in attaching addition
products to these two faces than there would be in the
case of the isomeric Olefine or in the case of Fig. 45.

The differences in chemical and physical characteristics which separate propylene and cyclo-propane are not very great, the principal difference being in regard to Potassium permanganate, for while Propylene reacts with this substance in dilute solution in contact with Sodium Carbonate, Cyclo-propane does not react with Potassium permanganate. Both compounds form addition products with the Halogen Acids and with Sulphuric Acid ; their Boiling points are reported as—

Propylene—48°

Cyclo-Propane—35° calculated

Propylene adds on Bromine readily, but Cyclo-propane *slowly*.

It must be admitted that there is considerable difficulty in deciding upon the configuration of cyclopropane as also in deciding which of the two Figs. 44 or 45 should be assigned to it.

It is submitted that if Fig. 45 is adopted the differences in the structure of the carbon framework are sufficient to explain the differences in Chemical and Physical Characteristics, and if Fig. 44 is adopted the position of the unsaturated faces on the opposing sides of the concavity would also materially affect the reactivity of the compound.

CYCLO-BUTANE. This substance can be synthesized from Cyclo-Butyl-Carboxylic Acid, but we do not find any direct evidence of the existence of a cyclic formation.

It can be converted into cyclo-pentane, but there does not appear to be any evidence of the conversion of any of these substances into compounds containing a Benzene Ring.

CYCLO-PENTANE is synthesized from Calcium Adipate, but there is no direct connection between this substance and compounds containing the Benzene Ring—the existence of a true ring in this compound appears open to doubt. Either of the two possible configurations shewn on page 115 may be adopted, and in the first case the two faces on opposite sides of the concavity will be so situated that addition products will be impossible. The second configuration, Fig. 63b seems, however, to be more in harmony with the stability of the substance.

CYCLO-HEPTANE AND CYCLO-OCTANE. In these compounds it is suggested that instead of a cyclic configuration, unsaturation is indicated, the unoccupied faces being situated at the opposite ends of the carbonoid aggregate.

CHAPTER XII.

CONCLUDING OBSERVATIONS.

The question of whether any other Investigator has already propounded any Theory of Atomic Form in connection with the Carbon Atom naturally deserves consideration.

It appears that some attempts have been made in this direction by Chemists abroad, but the papers on the subject are only to be found in Foreign Journals or Publications and no particulars are to be found in those Text Books in this country to which the Author has access.

Much of what appears in the foregoing pages is the result of a study of models of the Carbonoid and its aggregates, and it is difficult to explain by drawings alone all the features of these aggregates ; as it is only by inspection of the models and the groups of models that their peculiar configurations can be realised. It is submitted that some justification of the Theory of Atomic Form is to be found in the facts set forth in the preceding chapters, and that this view is supported by the way in which the carbon framework of the principal formulæ in which carbon takes a part are represented by groups and aggregates of the carbonoid.

I

It is remarkable that the characteristics of the Ethylene group, and the Benzene Nucleus should be represented by models of carbonoid aggregates, and that, at the same time, the right- and left-handed Isomerism and Law of Even Numbers should find their illustration, and possible explanation, in the models of carbonoid chains, while at the same time the crystalline forms of solid carbon are fully accounted for. Triphenyl-methane, Condensed Rings, and Cyclic Compounds are considered, and suggestions are made with regard to the structure of these compounds.

The consideration of the crystallization of carbon compounds, such as Carbon Dioxide, Benzene, Naphthalene, etc., may lead to difficulties. If the crystal form depends upon the configuration of the molecules of which the compound is composed, the models of the carbon framework should be of such a form that they can be built up into a space-lattice suitable for the required crystal. Very little progress has however been made in this direction.

In the case of a single element where the form of the atom is assumed, there should be no difficulty in forming a suitable space-lattice ; but where more than one element is involved in the molecule, as in the Hydrocarbons, we are met with the difficulty that we do not know the form of the other element nor what effect the Hydrogen or Oxygen of the compound may have on its power of crystallisation.

It is clear, however, that Oxygen possesses an unique power of linking together other elements so as to form crystalline compounds ; the carbonates, silicates, nitrates, phosphates, sulphates and other compounds

prove the large number of substances, with very definite crystalline forms, of which Oxygen forms a part.

It will be observed that throughout this book symbols representing double bonds have not been generally employed;— unsaturated molecules being treated as having unoccupied faces. It is of course impossible for any geometric solid figure to be united to another figure of the same or similar form by more than one of its faces, but it is quite likely that where the attached atom is of large size, compared with the atom to which it is attached, the base of the attached atom may extend beyond the face of the " *nuclear* " atom and may prevent the occupation of an adjoining face. The question of whether a particular face of an atom is available for occupation by another " attached " atom will depend upon the position which this face occupies in the molecule—the configuration of both the " nuclear " and the " attached " atoms, and sometimes on the axis of rotation of the molecule. The introduction of the idea of geometric form, provides new possibilities affecting the valency of the atoms.

With regard to the formation described as "*conjugated*" Double Bonds, of the form $C=C-C=C$ or

$$H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H \qquad \text{the addition of Bromine}$$
$$H \quad H \quad H \quad H$$
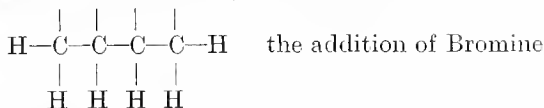
takes place at Nos. 1 and 4, thus :

$$\begin{array}{cccc} Br & & & Br \\ | & | & | & | \\ H-C-C-C-C-H \\ | & | & | & | \\ H & H & H & H \end{array}$$
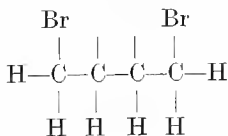
the so-called double bond being removed to the pair of
atoms, 2 and 3 above; this seems probable by reason of
the size of the Bromine Atom, which in some circum-
stances might be prevented from occupying the faces
of adjacent carbonoids.

The existence of the four unoccupied faces in juxta-
position is accompanied by an exaltation of the mole-
cular refraction which disappears on the removal of
the pair of unoccupied faces to the middle of the molecule.

In partial explanation of these features we notice
that a tetracarbonoid model when viewed from one
side, which we will call the front of the model, presents
two pairs of co-basal faces, Nos. 1—2 and 3—4, see
Fig. 46, p. 72b, but on the occupation of Nos. 1 and 4,
the remaining faces 2 and 3 do not present a pair of
faces in a satisfactory position to one another, the
pair being separated by a considerable space.

Another view of the model from the back shews
four faces arranged as shewn in Figs. 51 and 52,
p. 96.

On the occupation of the two faces at the top
and bottom of the figure, being Nos. 1 and 4 in the
foregoing formula, there remains a pair of co-basal
faces (unoccupied) in the middle, marked c and d in
Fig. 51, which may fairly represent the double bond in
the centre of the molecule.

Without being confident that this is the correct
solution of the problem, the carbonoid model shews

how a case of four adjacent unsaturated faces may be resolved into a single pair of faces on adjacent carbonoids united by the same base, and occupying the middle of the formula.

It is possible to design forms for the various elements with any number of faces from 4—excepting 7—up to at least 8, and the positions of these faces could be such as readily to give either 3 or 5 " available " faces, 4 or 6, etc., and as we have already shewn, the faces available for attachment may be limited to 1 or 2.

With regard to Cyclic Compounds, the point at issue in connection with these compounds (except those containing five or six carbons) is whether they are true ring structures or whether they have some other configuration, differing from the open chain compounds, in the form of the carbon framework and probably also in the arrangement of the attached Hydrogen. It is submitted that the variety of form of carbonoid aggregates enables a different carbon framework to be allotted to these compounds and thus provides for the differences of character which are observed.

In compounds containing more than six carbons symmetrical groups of carbonoids can be constructed which differ from the spiral chains allotted to the open chain compounds, but which may nevertheless represent cyclic compounds. Here again the variety of form obtainable by different combinations of carbonoids is noticeable.

The Theory of Atomic Form must accord with the classification of the Elements under the Periodic Law, and it is suggested that the various groups and subgroups into which the Elements are divided under this law are represented by different geometrical solid forms which are either the same or similar for atoms comprised in the same group.

In some cases the form may be the same, but the size of the atom may be different owing to an enlargement of its dimensions.   In other cases while the main features of the geometric form are retained and the number of faces remains the same, a change in one or more of the dimensions will produce a somewhat different figure with a larger size.   A complete change of form including a larger number of faces may represent a change from one group to another.

In order to verify these assumptions it is necessary that the forms should be ascertained of a considerable number of the Elements, including those belonging to the same group, a work of considerable difficulty.

Let us consider the case of Silicon—the Element so closely allied to Carbon and occupying the next place to it in Group IV. in the Table.   It seems probable that Silicon may have a similar form to Carbon, with a proportional enlargement of its dimensions.

It will be remembered that the face of the carbonoid is an isosceles triangle, where A—D = B—C.   Fig. No. 9.

Any alteration of A—D will result in an alteration of the size of the solid figure without altering the form of the atom.

It is immaterial what the unit of measurement may be. Let us assume that A—D, or B— C = 24, then the volume of the Carbonoid will be 1995·36.

Let us assume that the Siliconoid has a base and perpendicular enlarged by one-third, making it 24+8 = 32, then the volume of the Siliconoid will be 4729·6853.

The volumes of these two figures should stand to one another in the same ratios as the atomic weights of Carbon and Silicon. The following is the result :—

Mass of Carbonoid	Mass of Siliconoid	Atomic Weight of Carbon	Calculated Atomic Weight of Silicon
1995·36	4729·685	12	28·44

The atomic weight of Silicon in the latest estimation available is 28·25 ; an earlier estimation gave 28·4.

The closeness of this result is noteworthy, but it must be remembered that it has been obtained by an arbitrary addition of one-third to the base and perpendicular of the carbonoid, a simple proportion, but one for which there is at present no authority.

Attempts to arrive at the mass of Titanium by a similar increase in the dimensions of the carbonoid, have not shewn any agreement with the Atomic weight, but this element cannot be regarded as closely associated with Carbon or Silicon.

While an attempt has been made in this book to elucidate the form of the carbon atom, much difficulty and uncertainty surrounds the theory of Atomic Form when applied to other elements, and the consideration of these problems has necessarily been deferred.

Any attempt to apply the Theory of Atomic Form to the elements generally, brings us face to face with problems of some difficulty.

With regard to Atomic weight, Valency, and certain other properties, the first seven elements in the Periodic Table shew a sequence of some regularity, which points to the existence of a relationship between them by which each of these seven typical elements may be considered as dependent to some extent upon those which precede and follow it in the table, as for instance in the case of the following pair of triplets :

M X	Lithium	7.	$M X_4$	Carbon	12.
$M X_2$	Beryllium	9·1.	$M X_3$	Nitrogen	14.
$M X_3$	Boron	11.	$M X_2$	Oxygen	16.

but notwithstanding this interdependence, the characters of these elements differ widely and in many important points—particularly melting point.

The Fluorine group starting at 19 stands alone, but appears to be related to the six preceding items.

There is another triplet—Iron 56, Cobalt 59, Nickel 58·7, which fills an unique position in the table, and cannot be considered as being related in any similar way to the other members of the table, and in addition there is the Helium-Neon group, making eight groups in all which start from elements of low Atomic weight, and three that start from Iron and its congeners. Hydrogen stands alone and cannot very well be considered in our present state of knowledge as being associated with any one of these groups.

Can each of the interdependent elements have a separate geometric form of atom, on which its characteristics depend ? If so, there must be some principle involved which is applicable to all the eight elements and which ordains the regularities which are observable. At present we do not understand how these separate Forms can be allied to one another so as to produce the regular increments of Atomic weight, and the regular sequence of Valency.

The advances from the first to the second period in the table are associated with an increase of Atomic Weight which approximates closely to 16 in each case, with, however, this feature, that the principal divergencies from an increase of 16 is found in the middle member of each triplet in each case. Beryllium increases by a little over 15 to form Magnesium, and Nitrogen by about 17 to form Phosphorous.

From the second to the third period the increment is about 16 for the first triplet and about 20 for the second. Such increases cannot be reduced to any regular proportion of the Atomic weights with which the group commences.

In the case of Silicon, we have found that 1/3rd added to the dimensions of the Carbonoid produces a solid figure with the Atomic weight of Silicon, but if we were in a position to make a similar calculation for Oxygen, we should probably have to employ some entirely different proportion and so on for each member of the eight groups.

If, therefore, each of the elements has its own geometric form, how can the mass of the Atom be enlarged by the same quantity in each case, in order to produce the next item in the group ?

Another peculiarity of these groups is to be found in the way in which they divide into two series thus :

$$K\ 39 — Rb.\ 85·4 — C_s\ 133$$

Li 7—Na 23

$$Cu\ 63·6 — Ag\ 108 — Au\ 197·2$$
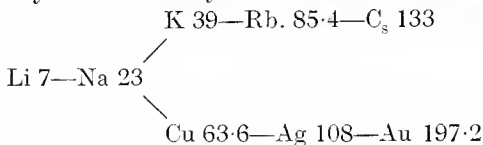
No explanations of these curious relationships are at present available.

Although these increases are generally so regular that the elements almost always retain the same order in the 3rd and 4th periods, they are evidently independent (so far as Atomic weight is concerned) of the groups that precede and follow them in the Periodic Table, the differences between consecutive elements becoming both greater and less in the later periods, and in two cases, Tellurium and Argon, the Atomic weights advancing beyond the position of the next group above it.

It is submitted that the Table of Atomic weights must be regarded as a record of a series of groups starting from the 11 elements above mentioned.

It is suggested that three problems lie before us viz. :—

(1) What are the relationships existing between the 11 elements referred to above ?

(2) What are the principles which determine the Atomic weights and other characteristics of each item in the several groups ? and in what way are they dependent upon one another ?

(3) What is the nature of the changes of form and character which arise with each increment in Atomic weight ?

The Theory of Atomic Form postulates that these problems can be answered by determining the geometric form of each of the 11 elements and by arriving at the changes in the dimensions and form thereof which produce the increments in Atomic Weight as we pass from one series to the next. Such changes may be produced by aggregations or additions of simpler forms, or by an increase in dimensions of some part of the geometric figure or by some other change of form, but we are still far from being able to present any comprehensive scheme or to submit forms suitable for any of the groups except Carbon.

In view, however, of the strong *a priori* grounds in favour of the view that the elements must possess geometric forms which have been already discussed in Chapter I., we submit that these problems deserve further study and consideration.

With regard to crystallization, it is suggested that three different kinds of aggregates should be acknowledged.

(1). The " *Filament* " where the molecules, as in Isoprene and the Rubbers, are merely linked to one another in a chain of indefinite length.

(2). The " *Network* " where the molecules are capable of being linked together in the form of a network, as in the case of Graphite, but do not build up a lattice in three dimensions.

(3). The " *Crystal* " where the molecules are built up in a definite geometric form dependent on, although not necessarily similar to, the forms of the atoms making up the molecule.

It is suggested that these distinctions should be borne in mind when considering the forms of atoms and molecules.

Attention is directed to the argument in favour of the Theory of Atomic Form which is based upon the inability of the present constitutional formulæ properly to represent some of the isomeric forms of compounds of three or more carbons.

The present formulæ are unable to represent the form of the carbon aggregates in cases where the isomerism is due to the special configuration of these aggregates. Instances of this kind are to be found in the three forms of Malic Acid and the five forms of Acids of the formula $C_4 H_6 O_2$ when only four are theoretically possible. In other cases where the Isomers are assumed to be represented by different arrangements of the attached Oxygen and Hydrogen, a critical study of the facts indicates that some other and more important differences of configuration are probably the causes of the differences in chemical and physical characters which these isomers display.

It is submitted that no satisfactory formulæ can be prepared, so long as the carbon atom is assumed to be spherical in form, and therefore unable to be built up into right- and left-handed forms for the carbon framework of compounds containing three or more carbons.

Attempts to get over this difficulty have been made by introducing the *trans* and *cis* formulæ in which the carbons are assumed to be arranged in a special manner relative to one another. The carbon atoms will however be unable to do this with any degree of stability unless they are themselves tetrahedra, or unless special and peculiar forces are acting between the spheres. We have no definite knowledge of the forces operating between the atoms of a carbon compound, which give rise to attraction and cohesion, but it is difficult to understand how any such force can act upon a system of spheres in such a way as to produce a stable configuration as depicted in some of our formulæ.

The idea that Electronic forces are responsible for the formation of carbon aggregates is not supported by chemical evidence.

Such forces are responsible for the behaviour of ions in solutions of electrolytes but they do not play any part in chemical reactions nor exercise directive power over the formation of isomeric compounds.

On the other hand, if the tetrahedral form of the carbon atom is adopted, we are placed in possession of a number of different forms of carbonoid aggregates, which enable all these isomers to be adequately represented and the isomerism explained.

The *trans* and *cis* formulæ are no doubt useful so far as they indicate that there is a change in the position of the carbon atoms relatively to one another, but they fail to indicate the true positions of the carbons in the molecule or the causes of the differences between the isomers.

Much remains to be done before the theory of Atomic Form can be fully elucidated. The phenomenon of Steric Hindrance, which is dealt with at considerable length in Stewart's *Stereochemistry* (1907) affords an extensive field for study, but is deferred in order that the main features of the Theory may be submitted.

It is well known that a large number of unsolved problems in Organic Chemistry await the result of further experiment and research. In view of this fact, it is submitted that the Theory of Atomic Form deserves the consideration of all who seek to unravel the mysteries of Atomic Affinity and Combination.

The object which we had in view at the commencement of this book, was to design the form of the Carbon Atom, and by preparing aggregates of the carbonoid in various arrangements, to compare these with the carbon framework of a variety of carbon compounds. To a certain extent this has now been done, and features of interest have been presented. The Author regrets that so much in connection with the subject is necessarily deferred, but feels it to be his duty to lay before the public the results so far obtained.

APPENDIX

It has been suggested to the Author that some information on the subject of model-making might be found helpful by those who desire to secure a more intimate knowledge of the carbonoid and its aggregates.

It is certainly very desirable that those who wish to obtain a clear understanding of the Theory of Atomic Form should have samples of the models before them, as it has been found impossible by drawings and photographs to exhibit all the features of the carbonoid-aggregates or to shew all the combinations of which they are capable.

Only one solid figure is required, viz., that of the carbonoid—of which a large number of plaster casts can be made from the same mould, all exactly alike. All the figures of carbon chains, rings, &c., are prepared by gluing the carbonoids together to make the form of carbonoid-aggregate required.

Materials. The models may be cast in Plaster of Paris or Portland Cement or some other substance which will quickly set when poured into a mould. The plaster casts are more easy to manipulate, but the cement models are stronger and more durable and less likely to be chipped or damaged. In the case of the

plaster models, the solid edges and corners of the car-
bonoid are easily damaged, but the cement models are
harder and more difficult to rub down so as to produce
uniform and satisfactory faces to the figure. Plaster
of Paris (best quality) appears to be the best material
by reason of the promptitude with which it sets.

The models made of Plaster of Paris may be
strenghtened by dipping them into a strong solution
of Size.

Size. The size of the Carbonoid Model will depend
upon one measurement, A D or B C, Fig. 9, p. 13. The
length of this line decides the size of the entire figure.
The Author has found a length of two inches a convenient
size. It would be easier to make accurate moulds to
a larger size, but the resulting casts would require more
material and in the case of rings of 60 carbonoids,
Fig. 19, p. 28b, would be unduly bulky. On the other
hand, if a smaller size be adopted, there is a difficulty
in securing sufficient accuracy in all the details of the
mould.

The Mould. The preparation of an accurate mould
is of special importance and requires great care. It is
best to commence by preparing a gauge in the form of
Fig. 9. It may be made out of ordinary sheet tin (or
more accurately tinned iron) and should be cut a trifle
larger than is desired and filed down to be strictly
accurate in all its proportions. From this gauge all
the measurements of the mould can be tested.

The mould will have three sides, the fourth side of
the carbonoid being represented by the top of the mould,
which will be left open and the plaster smoothed to a

level surface. Each of these three sides may be pre-
pared by cutting a piece of sheet tin into the three
forms shewn below.
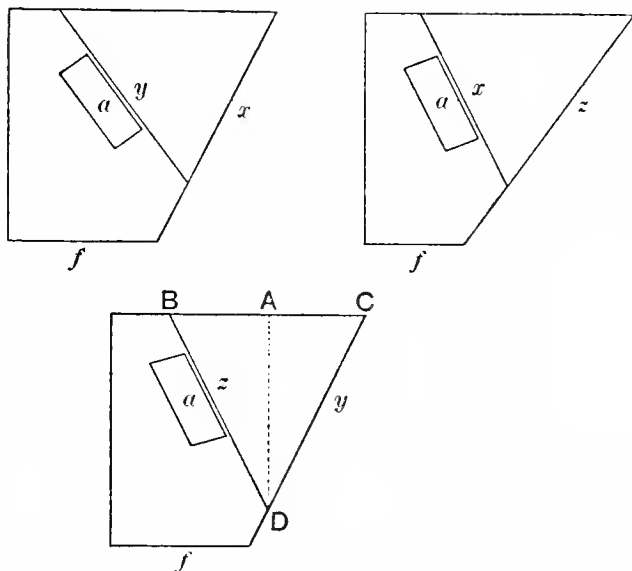
These drawings are made in a reduced size, but the pro-
portions are accurate.

The guides are marked *a*.

Lines of contact are marked *x x*, *y y* and *z z*.

If the pieces when soldered together do not give a perfectly
horizontal surface for the 4th side of the carbonoid the feet *f f f*
may be adjusted to give the desired result.

The strips of tinned metal marked (*a*) should be
soldered in their places as guides before putting the
pieces together. A small space must be allowed for
the thickness of the tin, so that the interior of the mould
may be exact.

J

The soldering together of the three sides of the mould is the most difficult operation, but is greatly assisted by having the guides in their right positions. All the soldering must be on the *out*side so that the interior may be exact ; the difficulty is in getting the first pair of sides soldered together at the right angle : to effect this an accurate model of the carbonoid in cardboard or wood should be prepared, and the mould can then be built up around the model.

It is well to make a small pin-hole at the bottom of the mould, in order to allow air to escape and prevent the models from being spoilt by bubbles at the bottom of the mould.

We recommend the use of tinplate, medium to strong in thickness, so that the mould may preserve its proper contour.

The importance of an accurate mould cannot be too strongly impressed upon the reader. If all the faces of the carbonoid are not quite equal, or if the two solid angles at A C and B D, Fig. 8, p. 13, are not exactly 1/6th of four right angles there will be a difficulty in obtaining correct figures of the benzenoid, carbon chains, &c., and the preparation of the ring of 60 carbonoids will be a matter of considerable difficulty.

Making the Models. The plaster should be thoroughly mixed and smooth, of the consistency of cream and be poured carefully into the mould, avoiding air bubbles. It is best to mix a small quantity freshly for each model, and to fill the mould to overflowing. As soon as the plaster begins to set, remove the surplus at the top of the mould with a knife and cut it down to a

surface level with the top of the mould. After standing until the plaster is quite set, invert the mould, and by tapping it on the outside the cast will be loosened and will fall out. It should be handled carefully and set aside until the next day, when it will be quite dry.

A level surface at the top of the mould can be secured by laying a smooth plate of metal on the top and squeezing out all surplus plaster, but there is danger of air-bubbles forming under the plate and causing irregularities in the surface.

After making the cast, the mould should be cleaned and the inside oiled, to prevent the plaster from sticking to the mould when next used.

When quite dry, the models may be rubbed down on a sheet of medium to fine glass paper laid on a flat board, to remove any irregularities, but care must be taken not to reduce the size of the model by too much rubbing.

Making the Aggregates. The carbonoids may be affixed to one another by any strong material. The Author has used ordinary glue, but care must be exercised not to apply too much. If pressed tightly together a small quantity of glue will make a good joint, but the most useful material appears to be " Necol " sold in tubes. It is always ready for use, dries quickly, makes a strong clean joint, and if carefully used will not run over or disfigure the aggregate ; the latter may require rubbing down with glass paper, and defects may be remedied by filling up holes, &c., with plaster.

K

To write on the models ordinary ink should not be used, but a small sable hair brush and Indian ink or lead pencil.

"Necol" may be used to strengthen the plaster model and prevent damage to the edges and points ; it should be applied as a kind of paint to the outside surface, smoothed down and allowed to dry.

INDEX